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## ERRATA.

## VOL. XCI (TRANS., 1907).

Page Line  
 1662 4\* for " $C_{12}H_{19}NClBr_2$ " read " $C_{10}H_{12}NClBr_2$ ."

## VOL. LXXXVI (ABSTR., 1904).

## PART I.

- 373 22 for "parasaccharie" read "parasaccharinic."  
 23 "saccharie" read "saccharinic."  
 25 "melusaccharate" read "melosaccharinate."  
 21\* "parasaccharate" "parasaccharinate."  
 19\* "saccharate" read "saccharinate."  
 19\* "isosaccharate" read "isosaccharinate."

\* From bottom.

dred substances; but our ignorance is correspondingly great of that of the blood colouring matters as well as of many coloured constituents of our own bodies: of the hair, the skin and the eye. The fullest recognition must be accorded, however, to recent investigations on the complex colouring matters of the blood and chlorophyll, which is distantly related to the former, associated with the names of Schunck, Nencki, Marchlewski, Küster and Willter.

In fine, the aid of synthetical chemistry is required in every action in arriving at a clear understanding of structure and of change. The methods at our disposal in the laboratory are doubtless altogether different from those which come into operation in the living world but chemists are already trying to effect changes in carbon compounds by means of so-called mild interactions, under conditions comparable with those which prevail in the living organism. It may suffice to refer to the development of a number of catalytic processes and to the comprehensive studies on the action of light on organic substances undertaken by Ciamician. In fact, an effort is already being made to co-operate with biology; it is clear that a section of the forces of organic chemistry is being directed once more towards the goal from which it set out. The information from biology was necessary during the past century while experimental methods and theories were being elaborated; now that our science is provided with a powerful armoury of analytical and synthetical weapons, chemists can once more renew the alliance both to their own honour and to the advantage of biology. Indeed, the prospect of obtaining a clearer insight into the wondrous series of processes which constitute animal and vegetable life may well lead the two sciences to work with definite purpose to a common end.

In order, as far as possible, to avoid mistakes in this difficult task and to shield ourselves from the disappointment which is the inevitable consequence of exaggerated hopes, we cannot do better than strive to imitate the great example of Faraday, who always, with rare acumen, directed his attention to actual phenomena without allowing himself to be influenced by preconceived opinion, and in his theoretical conceptions gave expression only to observed

CLXV.—*The Occurrence of Quercitol (Quercite) in  
Leaves of Chamaerops humilis.*

By HUGO MÜLLER.

WHEN collecting the materials for an article on Cellulose, which formed part of A. W. Hofmann's Report on the Chemistry at Vienna Exhibition,\* and treated of the application of cellulose in arts, I had occasion to devise a method for estimating the amount of available fibre contained in the various new papers proposed or in actual use.

Amongst the materials investigated, the leaves of *Chamaerops humilis*, the only European representative of the palm family, which at that time was imported from the Spanish province of Huelva to the country in some quantity and was used like esparto for making paper. During my examination of these leaves, I noticed that the aqueous extract, on becoming concentrated, deposited under favourable conditions a crystalline substance. This, on further investigation, proved to be quercitol, and I had subsequently an opportunity of preparing some quantity of it. The identity with quercitol from acorns was ascertained by its combustion, its chemical character, and melting point (230°), and the crystallographical measurement made at the tin of Prof. N. Story Maskelyne afforded further confirmation.

Quercitol had previously only been found in the acorn, and in a minute quantity in cork and the bark of the oak; its occurrence in the leaves of a distinct family of plants is therefore of some interest as we may hence expect it to be found more generally in the vegetable kingdom.

The quantity of quercitol yielded by the dry leaves of *Chamaerops humilis* amounted to 1.35 per cent., and, considering the simplicity of the process by which it can be obtained from them, these leaves may prove a more suitable source than the acorns. For the purpose of preparing the quercitol, the crushed leaves are extracted with boiling water; the resulting liquid is precipitated first with neutral and then with basic lead acetate. After removing any lead in the filtrate, the liquid is evaporated, when at the proper concentration the crystals of quercitol make their appearance.

With a special object in view, I recently repeated this operation with some fresh leaves of *Chamaerops humilis* kindly furnished by the Director of the Royal Gardens, Kew, and, in this case, a considerable quantity of the chlorides of potassium and sodium separated with the quercitol. I am indebted to Prof. W. H. Perkin for his

\* Bericht über die Entwicklung der Chemischen Industrie, 1877.

ring this quercitol from *Chamaetrops humilis* grown at Kew analysed the Schanck Laboratory, Manchester University, with the following result:

0.1410 gave 0.2268  $\text{CO}_2$  and 0.0935  $\text{H}_2\text{O}$ .  $\text{C} = 43.9$ ;  $\text{H} = 7.3$ .

$\text{C}_6\text{H}_{12}\text{O}_5$  requires  $\text{C} = 43.9$ ;  $\text{H} = 7.3$  per cent.

In 1904, Messrs. Power and Tutin (Trans., 85, 624) discovered in leaves of *Gymnoma sylvestre* (Bf.) (*Asclepiadaceae*) a new substance which had the composition, general properties, and constitution of quercitol, but proved to be its levorotatory modification. It was of course desirable to ascertain the specific rotation of the substance in arriving at a decision as to its nature. The methods at our disposal were those of Tutin, who kindly undertook to do this, and to be compared with those of that of d-quercitol of the acorn.

#### XVI.—Cocositol (Cocosite), a Constituent of the Leaves of "*Cocos nucifera*" and "*Cocos plumosa*."

By HUGO MÜLLER.

The occurrence of quercitol in the leaves of a palm was deemed of sufficient interest for it to be sought for in the leaves of other species of this family. The then (1875) Director of the Royal Gardens, Kew, Sir William Thiselton-Dyer, kindly gave me an opportunity of examining some of them and, in the first instance, supplied me with leaves of *Cocos plumosa* which could be conveniently spared at the

time. The green leaves were worked up in the manner indicated in the preceding paper on quercitol, but the result was negative, for not a trace of quercitol could be found. However, in the course of this examination the somewhat considerable basic-lead-acetate precipitate had been obtained and was decomposed in the usual manner with sulphuric acid. The resulting liquid, after concentration to a thin syrup, had been standing some time when some well-defined crystals made their appearance. These proved to be a new substance, resembling inositol in chemical character and having the same composition, but differing slightly in its physical properties.

This substance, which I propose for the present to name *cocosite*, is of sufficient interest to invite further investigation.

*The Occurrence of Cocosite in Cocos Leaves from Various Sources.*

Leaves of *Cocos plumosa* not being procurable, it was considered desirable to examine those of *Cocos nucifera* (the cocoa-nut palm) being more accessible, and a preliminary trial with such leaves, as obtained from Kew, having proved the presence of cocosite, a quantity of the dry leaves of this palm were procured from Jamaica.

Unfortunately, the yield was but small, and the investigation has subsequently to be suspended for want of material and from other causes.

Recently, however, I have again taken up this work, and in the present communication I offer an account of the results thus far obtained.

For the continuation of this research, it was, in the first instance, necessary to secure a further supply of cocosite, and I availed myself of an opportunity of importing the cocos leaves from Barbados, for which I am indebted to Mr. J. R. Bovell, Superintendent of the Agricultural Department at Bridgetown. The quantity of cocosite derived from about 50 kilos. of these leaves was, however, very small, and the percentage so much less than that I had formerly obtained from the Jamaica leaves that I concluded this depended probably on the particular period of vegetation in which the leaves had been gathered. In order to ascertain this, I made arrangements during the last two years for receiving leaves at certain periods of growth: some also from bearing and non-bearing trees. As even under the most favourable conditions the yield is but small, bulk samples of not more than 10 kilos. of the dry leaves were worked upon in each instance, this entailed a great deal of protracted and tedious work. With reference to further details, I may state here at once that no decisive results were, however, obtained.

Some of the samples yielded no cocosite, whilst others gave only traces, and at the best furnished very small quantities indeed of the desired substance.

In all these cases, the first part of the operation, namely, the extraction of the crushed leaves with water, was carried out for me in the laboratory, and, remembering the special conditions under which sorbitol is formed from the sap of the mountain-ash berries, it appeared well worth while to see whether the presence of cocosite did not perhaps depend on some fermentative change accidentally induced in the previous operations of 1878, but such change being precluded in the recent experiments this might account for the variable and unsatisfactory results here recorded. With this view, the decoction of a sample was exposed to the air in a flat dish and allowed to become thorough

before being worked up, but the result was entirely negative.

On the other hand, I repeated the original experiment with some fresh leaves of *Cocos plumosa*, which again were kindly supplied by the Director of Kew Gardens, and these yielded as before the oil in a very satisfactory manner and quantity, thus proving that the oil is contained ready formed in the growing leaf.

As the cocoas leaves received from Barbados having failed to furnish a adequate amount of cocosite, I had recourse to other sources, and accepted the kind offer of Colonel Prain, the present Director of Kew Gardens, to procure for me a supply of leaves from the Royal Botanic Garden at Sibpur, Calcutta. I am indebted to Captain Gage, Director, for a consignment of samples of leaves gathered in June, which I have lately finished working up.

The samples of leaves were designated as follows.

The leaves marked A are from the top of a tree cut down, of which a part is sent as well as some of the outer leaves. Those marked 1, 2, and 3 respectively are from three different trees, three leaves each, namely, a fully ripe leaf and a young leaf just expanded. The leaves marked 1 are from a tree that is in flower, but has no fruit on it. The particular tree is the variety called by the Bengalees "Shwet" meaning white cocoa-nut; N 2 are leaves from a tree that is in flower nor in fruit, and N 3 are leaves from a tree that is in flower and fruit.

Meanwhile I had also made arrangements for again obtaining a supply of leaves from Jamaica, as these had given such much more satisfactory results in 1878, and through the kindness of Mr. Sweett, the Director of the Public Gardens and Plantation at Kingston, I obtained a few months ago a quantity which is now being worked up. The following table shows the great variability in the amount of cocosite obtained from the various kinds of leaves which were worked upon in quantity or examined as samples.

The Barbados leaves, having yielded such altogether insignificant quantities, are not taken into consideration.

Leaves of <i>Cocos plumosa</i> from Kew.....	0.23	per cent.
" " <i>Cocos nucifera</i> , Jamaica, 1878	0.17	" "
" " " " " 1907	0.05	" "
V 1 " " " " Sibpur, Calcutta	0.03	" "
V 2 " " " " " "	0.03	" "
V 3 " " " " " "	0.04	" "
A " " " " " "	traces	

From this, it will be seen that the leaves of *Cocos plumosa* are the best, and next to them come the cocoa-nut palm leaves from Jamaica.



obtained in 1878, but those imported from that island this year only about one-third of the former.

On the other hand, out of the four samples from Calcutta contain about the same quantity, whilst the sample A ga traces.\* Quite recently, I have also completed some experiments on *Cocos nucifera* leaves from bearing and non-bearing trees, not from the Seychelles, but from neither of these have I obtained cocosite.

Otherwise, all these trials give no clue whatever as to the dependence of the amount of cocosite in the leaves on the part, vegetative condition or the season in which the leaves are gathered.

In the course of this work, the problem suggested itself that cocosite might be contained also in the coconut, and, as these are obtainable, several trials were made. The so-called milk and perisperm were examined. From 1 litre of the clear liquid obtained from fresh nuts a few centigrams of well-defined characteristic crystals of cocosite were obtained, but in 5 kilos. of the perisperm which was worked up for this purpose, no cocosite was found.

#### *Preparation of Cocosite from the Leaves.*

For the purpose of extracting the cocosite from the leaves, I follow in the main, until quite recently, the process indicated in the preface on quercitol, and which is the mode of proceeding generally adopted in the investigation of the aqueous extract of plants. As the palm leaves are very stiff and hard, they are first reduced by means of a chaff-cutter and crushed, and then extracted by successive boilings with water. The clear, brownish-yellow liquid thus obtained is then first precipitated with neutral lead acetate and, after filtered, completely precipitated with a solution of basic lead acetate, of which a very considerable quantity is required on account of a very large amount of sodium and potassium chloride contained in the leaves.

This latter, very bulky, yellow precipitate thus obtained is well washed with distilled water and decomposed with sulphuric acid. The filtrate from the lead sulphate is then evaporated on a water-bath or steam-bath to a thick syrup or nearly to dryness, during which process a little hydrochloric acid is given off and the liquid becomes very discoloured. On now redissolving this extract in cold water, a very considerable part, consisting of a dark brown, resinous substance mixed

\* The extracts of the Sibpur leaves had been evaporated down to the consistency of a thick treacle, and, after some months' standing, in those of 1, 2, and 3, rough crystals were noticed which proved to be cocosite. The extract A contained a larger amount of crystals, but they were found to be only the chlorides of calcium and sodium.

remains behind, and this occurs after repeating the evaporation on several times, hydrochloric acid being given off to the last. Evaporation is necessary in order to free the liquid as much as possible from a semi-gummy and a resinous matter which much impedes the separation of the coccosite.

In more recent operations, I have treated the basic precipitate with a small quantity of dilute acetic acid to produce an acid liquid, by means the greater part of the chlorine and silica is retained in the precipitate, whilst the coccosite is now left in the liquid, from which it can be easily removed by the usual means.

Though not very readily soluble in water, the coccosite separates slowly from the concentrated liquor, which requires to stand for some time unless the coccosite is present in some quantity. The action of the coccosite can, however, be accelerated by the addition of alcohol to the liquid whilst hot, when, on cooling, the coccosite immediately makes its appearance in more or less well-formed crystals. After recrystallisation and treatment with animal charcoal, are obtained in a pure state.

In the course of the further study of the chemical properties of coccosite I was led to the working out of a modification of the above process by which the troublesome precipitation with the lead was superseded. I found that by the addition of milk of lime to the hot decoction of the leaves a very large amount of a gum, resin-like substance and colouring matter, is thrown down, and, in some of the trials, to as much as 50 per cent. of the matter contained in the extract. After removing this by filtration, the liquid is concentrated by evaporation on a water-bath. A concentrated solution of baryta is now added and the boiling continued for some time.

The baryta at first produces a dark yellow precipitate, which on further addition is followed by a heavier and paler precipitate. It here be mentioned that the coccosite is mainly contained in the latter part of the precipitation. The baryta precipitate is filtered off whilst still hot and washed with hot water, then mixed with sufficient water, and carbon dioxide is passed into it until this is no longer absorbed. The liquid is now filtered off and concentrated by boiling, which causes the precipitation of the dissolved barium carbonate. When the proper concentration is reached, the coccosite separates in crystals, which are thus obtained colourless without the aid of animal charcoal, and after recrystallisation are chemically pure.\*

In order to test the efficacy of this method, a quantitative experiment was made by dissolving one gram of coccosite to a quantity, usually operated upon, of leaf extract which did not contain any coccosite, with the result that 0.92 gram of the coccosite was recovered.

Cocosite crystallises from water in beautiful, transparent crystals, which, under favourable conditions, may be obtained metre in diameter. It is not very soluble in cold water, and found that 100 c.c. of water at 15° dissolve 1.7 grams of cocosite, 100 c.c. of water at 100° dissolve 8.3 grams.

It is insoluble in methyl or ethyl alcohol, ether, benzene, chloroform, or any other of the usual solvents.

When heated on platinum foil, the crystals first decrepitate, melt, and take fire, burning with flame, like sugar, and charcoal. When carefully melted and not over-heated in a glass dish it forms a mobile, brown liquid, which, on cooling, suddenly solidifies and then bursts up into crystalline fragments.

The melting point was found to be at 345–350°, but this is close to the limits of the mercury thermometer, the determination will have to be repeated on a future occasion with other and more reliable means.\*

A saturated aqueous solution when tested exhibited no indication of optical activity.

On evaporating a hot solution, or on cooling a hot saturated solution, the cocosite separates in the characteristic form of short, prismatic crystals, which do not show any change when kept in the air at an elevated temperature; but, on the other hand, if a cold, saturated solution is gradually evaporated in a desiccator, crystals of a different habit appear; they are massive and long, prismatic, and on being removed and dried soon become opaque, white, and friable, in consequence of the transformation into an aggregate of many small crystals. This change also takes place when these crystals are introduced into hot water. I have not been able to satisfy myself whether this change is due to a loss of water of crystallisation or to a change of crystalline form.

I am indebted to Mr. T. V. Barker, B.A., B.Sc. (Oxon.), of the Mineralogical Dept., University Museum, Oxford, who has kindly undertaken the crystallographical examination of this and the other crystalline compounds which are described in this communication.

#### *Cocosite.*

System: monoclinic.

Ratios of the axes:  $a:b:c = 1.7942:1:0.7656$ ;  $\beta = 117^{\circ}12'$ .

Forms:  $m = \{110\}$ ,  $c = \{001\}$ ,  $o = \{111\}$ , and  $r = \{201\}$ .

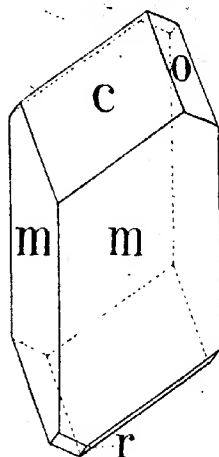
The habit of the crystals is shown in Fig. 1, the dominant forms being  $m - \{010\}$ , and  $c - \{001\}$ ;  $r$  was rarely present. The crystals afforded fairly good reflections, but rarely fell perfectly in zones.

\* Even mercury-thermometers filled with carbon dioxide and nitrogen seem to become untrustworthy after being used at these high temperatures.

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measurements were obtained from three selected crystals.

FIG. 1.



gle.	No. of observations.	Limits.	Mean.	Calculated.	Diff.
$\bar{1}10 : \bar{1}10$	8	$63^{\circ}58' - 64^{\circ}18'$	$64^{\circ} 9'$	—	—
$\bar{1}\bar{1}0 : 001$	9	$75\ 53 - 76\ 2$	$75\ 57$	—	—
$001 : \bar{1}\bar{1}1$	9	$43\ 35 - 44\ 17$	$44\ 5$	—	—
$\bar{1}\bar{1}1 : \bar{1}10$	8	$59\ 25 - 60\ 29$	$59\ 56$	$59^{\circ}58'$	$2'$
$\bar{1}11 : \bar{1}10$	4	$57\ 53 - 57\ 59$	$57\ 56$	$58\ 2$	$6$
$\bar{1}\bar{1}1 : \bar{2}01$	1	—	$44\ 39$	$44\ 26$	$13$
$\bar{2}01 : \bar{1}\bar{1}0$	1	—	$77\ 32$	$77\ 32$	$0$
$001 : \bar{2}01$	1	—	$51\ 22$	$51\ 13$	$9$
$\bar{1}\bar{1}1 : \bar{1}\bar{1}1$	1	—	$75\ 9$	$74\ 51$	$18$

age:  $\{001\}$  good.

$\beta$ : extinction on  $m = 33^{\circ}$  with edge  $mm$ . No characteristic  
ence figures are visible through  $c$  and  $m$ ; birefringence, strong;  
the mean lines is almost perpendicular to  $c - \{001\}$ .

fic gravity = 1.660; Mol. vol. = 108.5.

c axes:  $\chi = 10.085$ ,  $\psi = 5.6211$ ;  $\omega = 4.3035$ .

Two different preparations of cocosite were analysed:

I. 0.2215 gave 0.3220 CO<sub>2</sub> and 0.1357 H<sub>2</sub>O. C = 39.74

II. 0.2092 " 0.3046 CO<sub>2</sub> " 0.1289 H<sub>2</sub>O. C = 39.63

O<sub>2</sub>H<sub>2</sub>O<sub>2</sub> requires C = 40; H = 6.66 per cent.

A determination of the molecular weight by Beckmann was made with the following result.

To 15 c.c. of water boiling in the apparatus, 0.498 gram was added as a first charge, when a rise of 0.090° took place; addition of the second charge of 0.497 gram a further rise was observed.

The latter, which is experimentally the more trustworthy, gives 178.9 instead of 180 as required by the formula C<sub>8</sub>H<sub>12</sub>.

Cocosite forms feeble, but defined, and, in some cases, well crystallised compounds, as, for instance, with potassium, sodium, and it is precipitated by basic lead acetate, which affords a separating and concentrating it in the process of its isolation the aqueous extracts of plants.

When treated with acetic anhydride, it is converted into an acetate; with benzoyl chloride it forms a benzoate; with nitric acid a corresponding nitrate, and with sulphuric acid several acids.

Cocosite does not reduce Fehling's solution, but on boiling with ammoniacal silver nitrate solution and an alkali a silver mirror is produced.

An aqueous bromine solution appears to have very little action on it, and even in sunlight the bromine disappears very slowly. The addition of a little iron in the form of bromide or of ferrous sulphate decided reaction takes place.

Cocosite gives the well-known and characteristic inositol reaction of Scherer; on heating it with nitric acid, evaporating carefully, redissolving the residue in water, adding a solution of potassium chloride, and again evaporating it, a fine red coloration is produced.

#### *Cocosite and Potassium.*

When to a hot solution of cocosite (1.5 grams in 30 c.c. of water) an alcoholic solution of potassium ethoxide is added, the mixture deposits brilliant crystals which, however, were found to contain not a trace of potassium. On redissolving the crystals in water and off the alcohol, the same crystals of pure cocosite were again obtained on cooling. However, on dissolving the crystals once more in water, evaporating the liquid to about 100 c.c. and placing it in a desiccator over potassium hydroxide, a crop of beautiful, lustrous, short prismatic crystals was obtained, which somewhat resembled cocosite.

ed with alcohol, proved to be the desired potassium

to contain water of crystallisation, for the crystals, when  
 lose their lustre and become white. When heated on  
 it melts and chars, producing at the same time a peculiar  
 intumescence. On attempting to recrystallise it from  
 was decomposed, and again only pure cocosite crystallised  
 solution.

#### *Cocosite and Sodium.*

compound seems to be more stable, and is readily obtained on  
 hot solution with a methyl-alcoholic solution of sodium  
 . On cooling, well-defined crystals formed, which were  
 with alcohol and then kept for some time in a desiccator over  
 hydroxide.

lost 0.127  $\text{H}_2\text{O}$  at  $100^\circ$ ;  $\text{H}_2\text{O}=7.50$ ; on decomposing its  
 acetic acid and alcohol, 1.442 of cocosite was recovered,  
 an acetate gave 0.582  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=11.1$ .  
 $\text{Na}_2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=8.2$ ;  $\text{Na}=10.5$  per cent.

#### *Cocosite and Barium.*

on of barium hydroxide causes no precipitate in a cold  
 cocosite; but on heating the mixture and adding a hot  
 solution of barium hydroxide, it becomes turbid, and  
 white, granular precipitate is formed, which increases on boil-  
 solutions are of sufficient strength. This precipitate is  
 less in cold water than in hot, and on evaporating a solution  
 compound is obtained in small, but distinct, needle-shaped

#### *Cocosite and Calcium.*

addition of milk of lime to a solution of cocosite (1 in 200),  
 quantity of the calcium hydroxide is at first dissolved; but if  
 of it is added and the whole kept at the boiling point for  
 only a minute quantity of cocosite is found in the filtrate.  
 part of it is retained in combination with the lime. This  
 seemed to indicate a mode of preparing the cocosite from  
 extract, but it was subsequently found that from the complex  
 substances contained in the decoction of the leaves it is not  
 which is precipitated by the lime. Advantage is, however,  
 this in the mode of preparation of cocosite as previously

*Cocosite Hexa-acetate.*

Cocosite is but sparingly soluble in acetic anhydride. It was boiled with it for some time without apparently being acted upon. Adding a small quantity of anhydrous sodium acetate, or fused zinc chloride, immediate reaction sets in.

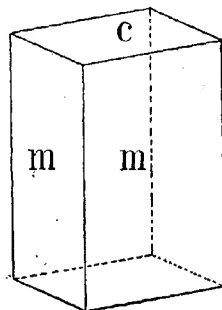
Five grams of powdered cocosite, 50 c.c. of acetic anhydride and 1.5 grams of zinc chloride, were boiled for several hours. The cocosite gradually dissolved, whilst glistening, small, prismatic crystals appeared, and towards the end of the operation the whole became a semi-liquid magma.

The product was boiled with water in order to hydrolyse it, then washed, and dried. It amounted to 11.3, 11.8, and 11.9 grams. The same results were obtained when the boiling was continued for 24 hours and zinc chloride was used. In the first operation, only 15 c.c. of acetic anhydride with five grams of sodium acetate was employed. The boiling continued for only two hours.

*Cocosite hexa-acetate* is sparingly soluble in alcohol and in other usual solvents, but from a hot solution in acetic anhydride it can be obtained in fine, prismatic crystals. It melts at about 100°C. In a tube at this temperature it sublimes apparently without decomposition. On boiling it with a methyl-alcoholic solution of baryta, it is decomposed into cocosite and acetic acid. It was analysed with the following result:

0.2003 gave 0.3673  $\text{CO}_2$  and 0.1018  $\text{H}_2\text{O}$ .  $\text{C} = 50.00$ ;  $\text{H} = 5.55$  per cent.  
 $\text{C}_6\text{H}_6(\text{C}_2\text{H}_3\text{O})_6$  requires  $\text{C} = 50.00$ ;  $\text{H} = 5.55$  per cent.

FIG. 2.

*Cocosite Hexa-acetate.*

were obtained from acetic anhydride.

noclinic.

a axes:  $a:b:c = 0.9222:1:1$ ;  $\beta = 97^{\circ}33'$ .

$\{110\}$ , and  $c = \{001\}$ ; the habit is shown in Fig. 2.

	No. of observations.	Limits.	Mean.	Calc.
$\{10\}$	12	$84^{\circ}49' - 84^{\circ}58'$	$84^{\circ}52'$	—
$\{110\}$	13	$84^{\circ}13' - 84^{\circ}33'$	$84^{\circ}26'$	—

none observable.

injection on  $m = 33^{\circ}$  with the edge  $mm$ . An optic axis  
nely through  $m$ ; birefringence, medium.

avity: mean of three concordant determinations =

vol.: 316.6.

#### *Cocosite Benzoate.*

g for an hour 3 grams of cocosite dissolved in 150 c.c. of  
8 c.c. of benzoyl chloride, which is gradually added alter-  
20 per cent. sodium hydroxide solution, a white, crystal-  
e, *cocosite benzoate*, formed, which weighed 1.7 grams.

r experiment, 0.5 gram of finely-powdered cocosite was  
c.c. of benzoyl chloride to boiling. A white substance  
can to be deposited on the walls of the tube, whilst  
loride was evolved. After heating for five hours, the  
contents of the tube were treated with a solution of  
onate to decompose the excess of benzoyl chloride. The  
is operation amounted to 1.8 grams, which is a very much  
stage than that of the former.

benzoate melts at a temperature above the limit of the  
ernometer, apparently without decomposition, and on  
mes a crystalline structure.

arkable for its very slight solubility in all the usual  
wo analysis gave:

and 69.06; H = 4.62 and 4.55.

$(C_7H_5O)_3O_6$  requires C = 70.28; H = 4.58 per cent.

#### *Cocosite Nitrate.*

odered cocosite dissolves in concentrated nitric acid with-  
gns of decomposition. In order to prepare this compound,  
ic acid was employed, in which the powdered cocosite dis-  
this at ease.

cocosite were gradually introduced into about 10 c.c.  
id, and the mixture was then gently warmed to



about 20°, when a clear solution was formed without any gas. To this solution fuming sulphuric acid was gradually added, which caused a white crystalline precipitate, accompanied by a considerable elevation of temperature to appear. When the latter had been added, the whole became a white, semi-liquid mass. After standing until quite cold, the mass was gradually introduced into water and ice.

The nitrate thus formed was collected and thoroughly washed with water. The above quantity of 4 grams thus yielded 1.5 grams of the nitrate.

This substance is very insoluble in most of the ordinary solvents, with the exception of boiling acetic anhydride, from which it dissolves on cooling in beautiful rhombohedra which probably belong to the rhombohedral system, since the angles between the faces are the same, namely, 75°55', the extinction in one direction being diagonal. When heated in a test-tube, it explodes without previous melting, filling the tube with nitrogen gas.

Two nitrogen determinations on this substance gave 14.64, which corresponds to that of the pentamethylenediamine, requires N = 14.64 per cent., but these results require confirmation. A quantity of about 3 grams having been kept for several days was found to have undergone almost complete decomposition. A few decigrams of the original nitrate remained, and, besides nitric acid, oxalic acid, and some oxidation products which, on rhodizonic acid reaction, the greater part of the residue of cocosite which had been regenerated by spontaneous hydrolysis.

#### *Cocosite Sulphonic Acids.*

If crystals of cocosite are introduced into fuming sulphuric acid, a reaction appears to take place, but, on gently warming, the surface becomes white, owing to the formation of a sulphonic acid. By raising the temperature, this is dissolved, and the crystals gradually disappear.

To facilitate the reaction, the cocosite was finely powdered. In one operation 3 grams were gradually introduced into 20 cc. of fuming sulphuric acid. Very slight elevation of temperature was sufficient to melt the thick mixture, which became liquid on placing it in a water bath. This liquid was poured on to a glass dish and left to cool. Lumps of ice were then added, and the liquid was gradually diluted with water without causing any perceptible elevation of temperature.

was then saturated with barium carbonate, filtered, and the water bath.

At various salts were thus obtained in a crystalline form, more insoluble than the other.

pected that some of the more insoluble compounds e barium sulphate (although well washed with water), this with dilute ammonium carbonate a small quantity on salt was finally obtained on evaporation.

#### *Action of Hydrogen Peroxide on Cocosite.*

eroxide seems to have no action on a solution of cocosite y temperature, but if, according to Fenton's method, a of ferrous sulphate is introduced, the peroxide becomes 3. The liquid at first turns yellow, and then on each of small quantities of hydrogen peroxide a dark purplish-on is produced, and the liquid becomes warm, without, evolution of gas if the temperature is kept low by cooling. While, the dark colour changes back into yellow, and finally shed when further addition no longer produces any color- e liquid is allowed to stand for a day or two, some w crystals of iron oxalate are deposited, and by means of calcium acetate free oxalic acid is removed. After liquid is evaporated in a vacuum. On redissolving the product in water and adding barium hydroxide, a itate is formed which gradually turns red, and after any yta has been removed with acetic or dilute hydrochloric a brilliant, red colour. This substance exhibits all the a rhodizate, and, like this, can be converted into a rom these results, it would appear that the products of are similar to those obtained by the action of nitric acid nd that there are compounds formed which are probably d to the tetrahydroxyquinone of Nietzki and Benckiser 18, 499). Further investigation and experiments on a rger scale are, however, required to make this a certainty.

#### *Action of Hydrobromic Acid on Cocosite.*

Further study of the chemical behaviour of cocosite, it was special interest to obtain some halogen derivatives. With some preliminary experiments were carried out by acting arated solution of hydrogen bromide in glacial acetic acid e hexa-acetate after the manner described by Perkin and (Trans., 1905, 87, 855) and employed by them with so ss. The results thus obtained established a close analogy

to those obtained with inosite hexa-acetate. These, carried out on a larger scale and are recorded in the paper (see below).

In 1887, C. Vincent and Delachanal (*Compt. rend.*, 1887, 105, 95) discovered and described a substance which they found in a small quantity in some mother liquor of quercitol which they obtained from acorns, and which they named quercin. This substance has not again been noticed since that time, but it bears a strong resemblance to cocosite that one would be tempted to put them as identical were it not that, according to Aschan (*Ber.*, 1889, 3389), not less than nine stereoisomeric forms of hexahydroxyhexane,  $C_6H_{12}O_6$ , of which inosite is the most probable, are possible. The probability of the identity of quercin is strongly supported by the crystallographical data given by Friedel (*Compt. rend.*, 1887, 105, 95) and these given by Friedel for cocosite. There is also the scyllit, discovered by Frerichs (*J. pr. Chem.*, 1858, [i], 73, 48), in the kidneys of certain plagiostomous fishes, which has quite recently been again prepared from the same source and more fully by Johannes Müller (*Ber.*, 1907, 40, 1821). This also bears a strong resemblance to quercin and cocosite, but it must be left to further investigation to decide whether they are actually identical.

## CLXVII.—*Inositol (Inosite).*

By HUGO MÜLLER.

THE difficulty which I experienced in securing a more abundant supply of cocosite (see preceding paper) for the continuation of the investigation led me to take up the study of the nearly identical stereoisomeric inosite, of which I happened to possess a small quantity. This I had prepared years ago from the mother liquor of cochineal, in which I found it to be contained in appreciable quantity, associated with tyrosine and guanine.

The behaviour of inosite would thus serve as a guide in the continuation of the investigation of the cocosite, which would be all the more valuable as, on account of the great scarcity of this substance, experiments with it have to be carried out with rather small quantities. In most cases, therefore, the experiments made with inosite are those made with cocosite.

part of the present communication is to give the results obtained in the study of the reaction of a solution of inosite in glacial acetic acid on inosite hexa-acetate. It was first obtained by Perkin and Simonsen (Trans., 1905; 87, 855), by bringing the hydrobromic acid into action affords a satisfactory and less destructive means than the employment of hydrobromic acid or the bromides of phosphorus. It was sent to Prof. W. H. Perkin, who had the compounds in this paper analysed for me at the Schunck Laboratory, University, and also to Mr. T. V. Barker, who undertook a graphical investigation.

#### *Inosite Hexa-acetate.*

The hexa-acetate used in this experiment was prepared by heating powdered inosite, in a flask provided with a long wide tube condenser, in quantities of 10 grams with 50 c.c. of acetic acid and 5 grams of fused zinc chloride. The reaction sets in with energy, and continues without the further application of heat. After to complete the operation, the contents of the flask were allowed to boil for about an hour, then allowed to cool, and the crystals repeatedly boiled with water. In this way a large quantity of hexa-acetate was invariably obtained. The crystals were obtained from toluene.

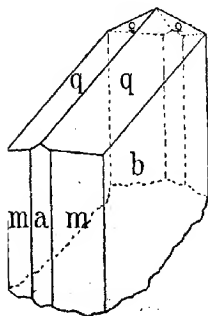
monoclinic.

cell axes:  $a : b : c = 1.1731 : 1.04395 ; \beta = 101^{\circ}58'$ .

faces:  $\{010\}$ ,  $q = \{011\}$ ,  $m = \{110\}$ ,  $a = \{100\}$ , and  $o = \{211\}$ .

shown in Fig. 1. The form  $o$  was observed on one

FIG. 1.



Angle.	Number of Observa- tions.	Limits.	Mean
$b : q = 010 : 011$	11	$66^{\circ} 1' - 68^{\circ} 40'$	$66^{\circ} 44'$
$q : q' = 011 : 0\bar{1}1$	5	$45^{\circ} 23' - 47^{\circ} 30'$	$46^{\circ} 23'$
$b : m = 010 : 110$	8	$39^{\circ} 6' - 43^{\circ} 20'$	$41^{\circ} 4'$
$a : m = 100 : 110$	6	$48^{\circ} 23' - 50^{\circ} 51'$	$48^{\circ} 59'$
$m : q = 110 : 011$	7	$64^{\circ} 16' - 65^{\circ} 27'$	$64^{\circ} 59'$
$q : m' = 011 : 110$	7	$79^{\circ} 21' - 80^{\circ} 49'$	$79^{\circ} 58'$
$b : o = 010 : 211$	1	—	$67^{\circ} 41'$
$o : o' = 211 : 2\bar{1}1$	1	—	circa $4^{\circ}$
$q : o = 011 : 211$	1	—	" $3^{\circ}$
$o : o' = 211 : \bar{1}00$	2	—	" $6^{\circ}$

Cleavage : none observable.

Optics : axial plane, normal to the symmetry plane wide; the first negative mean line makes an angle with the vertical axis in the acute angle  $\beta$ ; birefringence,  $m$

Specific gravity = 1.271. Mol. vol. = 340.04.

Topic axes :  $\chi = 10.286$ ,  $\psi = 8.7682$ ,  $\omega = 3.8539$ .

This hexa-acetate, after recrystallisation from benzene, was now heated in quantities varying from 20 to 40 gr. in test-tubes with 50 c.c. or 100 c.c. respectively of glacial acetic acid saturated at  $0^{\circ}$  with hydrogen bromide, for eight hours, then for another eight hours at  $150^{\circ}$ , and finally allowed to cool.

No pressure was noticed on opening the tubes, and on pouring the contents into water, a thick, white, semi-liquid mass separated, which gradually became nearly solid. On heating this with water, a heavy, almost colourless liquid which on cooling again solidified. This mass was now treated with cold alcohol, which dissolved the solid part, and left a white, chalky, indistinct, crystalline substance.

It was soon recognised that this was a mixture of several substances, the complete separation of which proved subsequently to be of great difficulty, and became, in fact, a most tedious process.

The part dissolved in the alcohol consisted mainly of a substance, insoluble in water, whilst another portion, which was retained in the aqueous acetic acid liquor, was obtained as a white, almost colourless, but amorphous, substance very soluble in water.

This multiplicity of substances formed in this reaction was somewhat embarrassing, and some special experiments were consequently made with the view of ascertaining whether the degree of temperature, or time of reaction, had any influence on the results.

many derivatives. These experiments, however, led to it and it became necessary subsequently to work up large quantities of material in order to obtain the facts in sufficient quantities for further examination.

In the operations, the contents of the tubes, after being washed, were distilled in a vacuum in order to remove the excess of hydrobromic acid, and it was then a small quantity of an oily liquid passed over with the distillate, which had the odour and other properties of it.

Further treatment of the white, chalky, crystalline product, from a suitable solvent was the only means of separation of its components, and after testing various solvents as alcohol, acetone, benzene, toluene, and glacial acetic acid, alcohol proved in the end the most advantageous. Hot alcohol dissolves the substance, but, on cooling, a large part of it separates as a crystalline magma consisting of small crystals. If, however, a very large quantity of alcohol, 50 parts, is used, small, white, indistinct crystals

which are followed by scaly crystals, and then by needles, make their appearance, but there are no very large crystals. The first only partial separation is attainable by washing with alcohol. If the crystallisation and removing immediately by filtration through a suitably warmed filter be repeated, another form sets in. By repeating this process the separation is finally effected.

The white, and indistinct crystals, which separate first as the mother-liquor, are *monobromoinosite penta-acetate*, the scaly and the needles are two isomeric forms of *dibromoinosite tetra-acetate*; the needles, a more soluble substance, crystallising in needles, is the alcoholic mother-liquor, but it has not yet been obtained entirely pure for analysis.

#### *Monobromoinosite Penta-acetate.*

It is deposited from its solution in the form of minute, white crystals, which melt at  $240^{\circ}$ , and on cooling form a solid mass. It is insoluble in water; but soluble in benzene, chloroform, acetone, or glacial acetic acid, especially when diluted with alcohol it is very sparingly soluble, but more readily so.

It was found that 0.5 gram required 75 c.c. of boiling alcohol to dissolve it, whilst 100 c.c. of the saturated solution at  $20^{\circ}$  only contained 0.015 gram. With a solution of sodium methoxide, it becomes a deep orange-

brown, and is decomposed by it on boiling. The solution reduces Fehling's solution. When heated with alcohol in a sealed tube at  $100^{\circ}$ , it gradually dissolves and the colourless product is readily soluble in water, but has been separated from the ammonium acetate and obtained in fine condition.

When acted on by zinc dust a reduction product (p. 1791). On analysis:

0.1852 gave 0.2873  $\text{CO}_2$  and 0.770  $\text{H}_2\text{O}$ .  $\text{C} = 42.3$ ;

0.2843 „ 0.1209  $\text{AgBr}$ .  $\text{Br} = 18.0$ .

$\text{C}_6\text{H}_6\text{Br}(\text{O}\cdot\text{CO}\cdot\text{CH}_3)_5$  requires  $\text{C} = 42.4$ ;  $\text{H} = 4.6$ ;  $\text{Br} = 18.0$ .

#### *Dibromoinosite Tetra-acetate.*

When quite pure, this substance can be obtained from solution in remarkably fine transparent crystals of  $\frac{1}{8}$  mm. in diameter. It melts at  $140^{\circ}$  to a clear liquid, which is a glass-like mass without any sign of crystallization. Topically it begins to crystallize and large, distinct crystals are formed. It is insoluble in water, but soluble in glacial acetic acid, chloroform, or acetone, especially when heated. It is soluble in alcohol at  $20^{\circ}$  dissolve 1.0 gram and 100 c.c. of alcohol dissolve 62.0 grams.

The hot alcoholic solution is a powerful solvent for compounds formed along with it by the action of hydrogen inositol hexa-acetate. When boiled with alcoholic potassium solution turns a deep orange-brown colour and reduces it. Alcoholic ammonia decomposes it gradually, even without causing any coloration, and the presence of this is indicated by the addition of silver nitrate.

When acted on by zinc dust, it is decomposed into phenol (p. 1790). On analysis:

0.2237 gave 0.2861  $\text{CO}_2$  and 0.0726  $\text{H}_2\text{O}$ .  $\text{C} = 34.9$ ;

0.2207 „ 0.1740  $\text{AgBr}$ .  $\text{Br} = 33.6$ .

$\text{C}_6\text{H}_6\text{Br}_2(\text{O}\cdot\text{CO}\cdot\text{CH}_3)_4$  requires  $\text{C} = 35.5$ ;  $\text{H} = 3.8$ ;  $\text{Br} = 33.6$ .

System: anorthic.

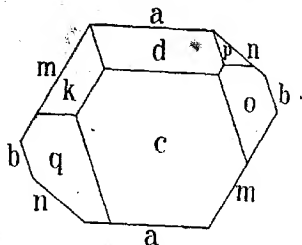
Ratios of the axes:  $a:b:c = 1.0644:1.09153$   
 $\beta = 116^{\circ}7'$ ,  $\gamma = 74^{\circ}3'$ .

Forms:  $b = \{010\}$ ,  $m = \{110\}$ ,  $a = \{100\}$ ,  $n = \{1\bar{1}0\}$ ,  
 $c = \{001\}$ ,  $q = \{0\bar{1}1\}$ ,  $p = \{1\bar{1}1\}$ ,  $d = \{101\}$ ,  $k = \{1\bar{1}1\}$ ,  
 and  $e = \{704\}$ .

The habit of the crystals was slightly prismatic, the

ating. Of the remaining forms, *d*, *k*, *q*, and *n* were considerable size, whilst *o*, *p*, and *b* were more subordinate; and *e* and *x* were observed but once (Fig. 2 is a projection of the prism zone).

FIG. 2.



No. of observations.	Limits.	Mean.	Calc.	Diff.
11	47°36'—48° 2'	47°49'	47°44'	5'
20	49 33—50 6	49 47	—	—
17	41 44—42 17	42 2	—	—
12	40 2—40 33	40 23	40 27	4
12	39 33—39 42	39 38	39 39	1
18	33 0—33 24	33 9	33 4	5
19	47 12—47 40	47 23	47 34	11
15	59 39—59 59	59 49	59 42	7
3	72 37—72 44	72 42	72 43	1
1	—	36 49	36 55	6
3	29 43—29 54	29 51	29 54	3
13	48 15—48 40	48 32	48 34	2
9	64 39—64 46	64 44	64 37	7
6	66 37—66 57	66 42	66 49	7
12	43 25—43 44	43 31	43 28	3
10	47 36—47 49	47 43	47 52	9
9	38 40—38 59	38 45	38 40	5
24	59 11—59 30	59 17	—	—
15	65 14—65 51	65 28	65 34	6
15	54 53—55 25	55 14	55 9	5
14	93 3—93 19	93 11	93 20	9
4	69 33—69 38	69 36	69 33	3
7	79 37—80 11	79 55	79 45	10
2	31 5—31 8	31 6	31 9	3
2	68 51—69 2	68 57	69 6	9
5	99 56—100 20	100 7	100 15	8



Angle.	No. of observations.	Limits.	Mean.	Calc.
$a : c = 100 : 001$	24	67.39 — 67.56	67.48	—
$c : d = 001 : 101$	16	47.53 — 48.27	48.9	—
$d : a' = 101 : 100$	16	63.50 — 64.19	64.2	61.3
$c : c = 001 : 704$	1	—	72.68	72.23
$a : q = 100 : 011$	13	63.25 — 63.52	63.37	63.43
$q : k = 011 : 111$	13	44.55 — 45.21	45.7	45.8
$k : a' = 111 : 100$	10	71.1 — 71.20	71.12	71.9
$n' : o = 110 : 011$	17	66.2 — 66.15	66.9	66.12
$n : c = 110 : 001$	10	87.10 — 87.24	87.18	87.19
$c : p = 001 : 111$	1	—	53.30	53.21
$p : n' = 111 : 110$	1	—	59.7	59.20
$c : n' = 001 : 110$	9	92.38 — 92.53	92.44	92.41
$n : q = 110 : 011$	12	50.44 — 51.6	50.55	50.55
$q : d = 011 : 101$	10	72.23 — 72.44	72.38	72.36
$d : n' = 101 : 110$	10	56.18 — 56.29	56.23	56.29
$q : x = 011 : 5 : 7-12$	1	—	27.37	27.53
$n : k = 110 : 111$	10	85.29 — 85.37	85.35	85.31
$p : k = 011 : 111$	10	87.57 — 88.10	88.1	88.11
$q : p = 011 : 111$	2	94.17 — 94.18	94.17	94.23

Cleavage: perfect parallel to  $a - (100)$ .

Optics: extinction on  $a$  makes an angle of  $4^\circ$  with the edge  $a$  on  $m$ , an angle of  $17^\circ$  with the same edge; the extinction on  $o$  is with the edge  $oa$ . An optic axis emerges obliquely through  $d$ . Birefringence is strong.

Specific gravity: two concordant determinations gave the value: Sp. gr.  $18^\circ/4^\circ = 1.713$ . Mol. vol. = 276.74.

Topic axes:  $\chi = 7.4623$ ,  $\psi = 7.0108$ ,  $\omega = 6.4169$ .

#### *Dibrominosite Tetra-acetate; Scaly Modification.*

The main difference of this isomeric modification from that described consists in its crystalline form and in the less degree of solubility in the various solvents. It invariably crystallises from solvents in glistening, thin scales; but under favourable conditions be obtained from a solution in toluene in more defined crystals.

It melts at  $235^\circ$  to a clear liquid, which on cooling becomes foliated, crystalline solid.

100 c.c. of a saturated solution in absolute alcohol at  $20^\circ$  contains only 0.18 gram, whilst 100 c.c. of boiling absolute alcohol dissolves 3.6 grams.

alcoholic soda, even in the cold, causes a deep orange-brown color, and readily decomposes it on boiling. The solution gives a positive reaction with Fehling's solution. On analysis:

0.14 gave 0.3031  $\text{CO}_2$  and 0.0781  $\text{H}_2\text{O}$ .  $\text{C} = 35.7$ ;  $\text{H} = 3.8$ .

0.71 " 0.2655  $\text{AgBr}$ ;  $\text{Br} = 33.6$ .

$\text{Br}_3(\text{O} \cdot \text{CO} \cdot \text{CH}_2)_2$  requires  $\text{C} = 35.5$ ;  $\text{H} = 3.8$ ;  $\text{Br} = 33.7$  per cent.

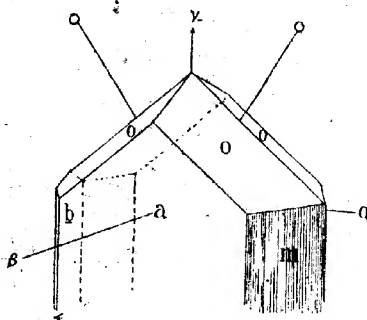
This modification generally crystallises in very small, slender scales, unsuited for crystallographic investigation, but a measurable specimen was finally obtained by slowly cooling a toluene solution. The crystal system: orthorhombic (holo-axial).

Ratio of the axes:  $a : b : c = 2.790 : 1 : 0.758$ .

Forms:  $a = \{100\}$ ,  $o = \{111\}$ ,  $m = \{110\}$ ,  $b = \{010\}$ , and  $n = \{430\}$ .

The habit is shown in Fig. 3; the prism zone was characterised

FIG. 3.



by a series of vicinal and curved faces, especially at the positive end of axis  $b$ . The form  $b$  always consisted of a single face  $\{010\}$ , and as crystals were never doubly terminated they may therefore be considered as axial. The form  $n$  was only observed once.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$a = 100 : 110$	5	$70^\circ 11' - 70^\circ 31'$	$70^\circ 17'$	—
$a = 100 : 430$	1	—	64 32	$64^\circ 28'$
$a = 111 : 111$	6	$71^\circ 56' - 72^\circ 42'$	72 22	—
$a = 111 : 111$	2	$25^\circ 37' - 26^\circ 8'$	25 52	24 26
$a = 111 : 100$	1	—	78 19	77 47
$a = 111 : 111$	2	$77^\circ 53' - 78^\circ 18'$	78 5	77 41
$a = 111 : 110$	1	—	51 1	51 10

Cleavage: perfect parallel to  $a$ , fairly good parallel to  $m$ .

Optics: axial plane parallel to  $a$ ; first positive mean line to  $c - (001)$ ; axial angle very wide; birefringence strong.

Sp. gr.  $17^{\circ}/4^{\circ} = 1.693$ . Mol. vol. = 280.01.

Topic axes:  $\chi = 14.220$ ,  $\psi = 5.097$ ,  $\omega = 3.863$ .

Up to the present, there is no indication of the formation of a higher brominated derivative than the dibromo-tetra-acetate. Inositol hexa-acetate is treated with excess of hydrogen bromide at  $150^{\circ}$ .

#### *Inositol Dibromohydrin.*

In the course of the earlier experiments, when dealing with the viscous part extracted by cold alcohol from the original crude product, it was noticed that on boiling it for some time with water for the purpose of removing the last traces of hydrobromic and acetic acid, it gradually dissolved. On evaporating the resulting liquid and allowing it to stand for some time, a crystalline substance separated from the syrupy mother liquor.

The same substance was also obtained when the aqueous mother liquor of the original product referred to above as containing an amorphous substance was repeatedly evaporated in a vacuum, re-dissolved to remove all hydrobromic and acetic acid, and the resulting thick liquid allowed to stand for some time.

The crystalline substance, after being freed as much as possible from the mother liquor by means of a suction filter and pressed between bibulous paper, was crystallised from water, and thus obtained in remarkably fine massive crystals which are quite colourless and of great brilliancy.

This substance is *inositol dibromohydrin*, and is evidently the product of hydrolysis of a dibromoinositol acetate. It melts at  $210^{\circ}$  with partial decomposition, becoming brown and giving off hydrogen bromide. It is readily soluble in water, less so in alcohol or in acetic acid, and insoluble in ether, benzene, or acetone.

100 c.c. of a saturated solution in water at  $20^{\circ}$  contain 3.15 g. and 100 c.c. of a boiling aqueous solution contain 60.00 g. 100 c.c. of a saturated solution in absolute alcohol at  $20^{\circ}$  contain 0.55 gram, whilst 100 c.c. of a boiling solution in absolute alcohol contain 6.00 grams.

Silver nitrate added to the aqueous solution gives after a while a slight turbidity, which increases on boiling. Caustic alkalis produce a dark brown coloration on boiling, and Fehling's solution is reduced by it. On analysis:

0.1876 gave 0.1634  $\text{CO}_2$  and 0.0577  $\text{H}_2\text{O}$ . C = 23.7; H = 3.4.

0.2095 „ 0.1801  $\text{CO}_2$  „ 0.0570  $\text{H}_2\text{O}$ . C = 23.4; H = 3.0.

gave 0.1353 CO<sub>2</sub> and 0.0479 H<sub>2</sub>O. C=23.7; H=3.4.

" 0.6471 AgBr. Br=52.2.

" 0.3880 AgBr. Br=52.4.

<sup>10</sup>O<sub>4</sub>Br<sub>2</sub> requires C=23.5; H=3.3; Br=52.2 per cent.

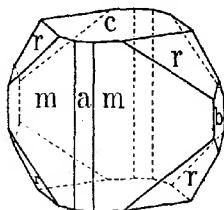
: orthorhombic.

of the axes:  $a:b:c=0.7726:1:0.7654$ .

:  $m=\{110\}$ ,  $c=\{001\}$ ,  $r=\{121\}$ ,  $b=\{010\}$ , and  $a=\{100\}$ .

abit was generally tabular, parallel to the basal plane; a few

FIG. 4.



however, were considerably elongated along the vertical axis. A crystal is shown in Fig. 4.

Angle.	No. of observations.	Limits.	Mean.	Calc.	Diff.
10 : 100	22	37°21' — 38° 0'	37°37'	37°41'	4'
10 : 010	24	52 7 — 53 3	52 22	52 18	4
11 : 001	10	61 11 — 61 21	61 15	61 16	1
11 : 121	11	122 10 — 122 53	122 32	122 31	1
121 : 100	23	61 8 — 61 58	61 32	61 33	1
121 : 121	13	56 36 — 57 7	56 52	56 54	2
121 : 010	17	42 21 — 42 52	42 37	42 36	1
121 : 121	5	84 56 — 85 31	85 15	85 12	3
110 : 121	8	33 40 — 34 42	34 7	34 12	5
$r : [cr]$	5	65 37 — 66 11	65 50	65 49	1

fundamental angles used were:  $r:a=61^{\circ}33'$ ,  $r:c=61^{\circ}16'$ , these are the means of all the angles in the two zones. The prism faces fall in the zone  $ab$ , and seem to be always vicinal; a good agreement between the observed and calculated angles is not obtained when the prism angles are used as fundamental angles.

No good cleavage was observed.

Optical properties: the crystals are biaxial, which proves substance, although pseudo-tetragonal, is really orthorhombic. First mean line is normal to the pinacoid,  $a = (100)$ , and is Plane of the optic axes  $b = (010)$ ; birefringence, strong;  $d\rho < v$ .

Two plates were ground, perpendicular to the acute and bisectrices respectively, and the axial angle was calculated from observations of  $2H_a$  and  $2H_o$  in cedar oil, sodium light being  $2E = 67^\circ 30'$ .

Specific gravity, two determinations were made: mean, D. 2.337. Mol. vol. = 130.94.

Topic axes:  $\chi = 4.6741$ ,  $\psi = 6.0495$ ,  $\omega = 4.6307$ .

It was found that the brominated inosite hexa-acetate is hydrolysed by boiling with hydrochloric or hydrobromic acid, and it seems probable that during the action of hydrobromic acid on the hexa-acetate some of the brominated hexa-acetate formed is hydrolysed, and that, in fact, the viscid part (insoluble in water) of the product is a derivative intermediate between the dibromohydrin and inosite dibromohydrin.

As, however, this viscid compound could not be obtained in a condition fit for analysis, this must for the present remain a substance.

This also applies to the substance contained in the final mother liquor, which is obtained in the form of a colourless or slightly yellow substance, resembling gum arabic and containing bromine, but in what relation it stands to the crystallised bromohydrin still to be ascertained.

#### *Products of Debromination by Means of Zinc-Dust.*

Having now obtained some of the bromo-derivatives in a crystalline form, their further examination could be proceeded with, a study of their behaviour towards reducing agents naturally suggesting itself. As a somewhat larger quantity of the dibromo-tetra-acetate, crystallising in massive crystals, was at disposal, this was taken first.

In a small retort, connected with a condenser, 5 grams of the crystals were dissolved in 30 c.c. glacial acetic acid and to this solution 5 grams of zinc dust were gradually added. No hydrogen was given off, but a reaction was indicated by the agglomeration of the zinc dust particles, and the presence of bromine in the solution could soon be detected by silver nitrate. The reaction was finally assisted by the application of a minute gas flame, the operation discontinued as soon as the addition of water to the

taken from the retort no longer caused a precipitate of substance. The contents of the retort were then mixed with water, and the residue (mainly cadmium) of the zinc dust

was then precipitated with a hot solution of silver. The filtrate from the silver bromide treated with hydrogen removed the zinc. On finally evaporating the liquid, there was left except a trace of zinc bromide. The whole of the substance acted on had thus disappeared.

On the evaporation of the liquid, there was besides that of a distinct phenolic odour perceptible, and consequently on repeating the experiment with a fresh quantity of the substance from the retort, after the treatment with zinc dust, were mixed with water and distilled. From the milky distillate passed over, a heavy oil separated which had the general character of phenol, and tribromophenol and phenyl benzoate were formed; it failed, however, to give satisfactory colour tests with ferric chloride and bleaching powder solution. Subsequently it was identified that this was caused by the presence of acetic acid. In a second experiment, the aqueous liquid remaining after distillation was again treated with silver acetate to remove the bromine, then with hydrogen sulphide to remove the zinc, and finally evaporated, leaving a scaly form of the dibromo-tetra-acetate to the residue.

On repeating the experiment, the experiment was carried out at a somewhat lower temperature on account of the more sparing solubility of the substance, but the result was precisely the same as in the first.

It seems then to be the only product of this reaction, and no other substance could be detected which might indicate the intermediates of the process which obviously must intervene.

The reaction presents some features of considerable interest. As mentioned, the dibromo-tetra-acetates on prolonged boiling, such as hydrochloric or hydrobromic, are hydrolysed, but it is found that with glacial acetic acid no perceptible change is produced.

The addition of zinc dust to the latter, however, even at a low temperature, not only induces the hydrolysis, but, in the act of attacking the bromine, breaks down the inosite molecule to

It is now a matter of special interest to study the behaviour of the monobromo-penta-acetate under the same treatment, and for this purpose 5 grams of the substance with 30 c.c. of glacial acetic acid were introduced into a retort and 5 grams of zinc dust stirred mixture; but as the substance is only slightly soluble, the

retort was gently warmed. Very little hydrogen was given; the substance gradually dissolved. After the lapse of six days the retort was allowed to cool, when it was noticed that the substance remained liquid, an indication that a reaction had taken place.

The addition of water now caused the separation of a crystalline substance which, on warming, melted and formed an oil, which again became crystalline on cooling. After reprecipitating it from dilute alcohol, it separated in soft, slender, prismatic crystals melting at 95°. This substance is readily soluble in alcohol as well as in water. It was dried in an evacuated desiccator over phosphoric acid:

0.1214 gave 0.2380  $\text{CO}_2$  and 0.0663  $\text{H}_2\text{O}$ .  $\text{C} = 53.4$ ;  $\text{H} = 5.9$ .

Average of three analyses:  $\text{C} = 53.3$ ;  $\text{H} = 5.9$ .

$\text{C}_{14}\text{H}_{18}\text{O}_8$  requires  $\text{C} = 53.5$ ;  $\text{H} = 5.7$  per cent.

Accordingly, we must assume that in this case the substance,  $\text{C}_{16}\text{H}_{21}\text{O}_{10}\text{Br}$ , is reduced to  $\text{C}_{16}\text{H}_{22}\text{O}_{10}$ , and this is the structure of acetic acid.

To test this view, an exact determination of the acetyl value was required, which, however, had to be postponed on account of lack of material.

In the mother liquor of this substance, another compound was found, which separates from the aqueous solution on concentration, leaving a colourless, heavy oil remaining liquid at the ordinary temperature for some time and then becoming a crystalline solid. This substance also awaits further examination.

#### *Inosite and Hydrogen Peroxide.*

The description given under the heading, "Action of Hydrogen Peroxide on Cocosite," in the preceding paper (p. 1779), applies to every detail to what takes place when inosite is submitted to the same treatment. The transient, deep purple-blue coloration appears in the same manner, and finally a stage is reached when further addition of hydrogen peroxide no longer produces this coloration. No carbon dioxide is evolved if the addition of the dilute hydrogen peroxide is made in small quantities, and time allowed for the appearance of the colour in the intervals. Some oxalic acid is present, which was removed by adding a solution of calcium acetate, and after filtration the liquid was concentrated in a vacuum. By this time it had become coloured, and in the course of a few days, after exposure to the air, had turned quite dark. On evaporating it further on a water-bath and allowing it to stand in a desiccator, it became colourless, no signs of crystallisation appeared. Its solution readily reduced Fehling's solution, and the characteristic barium rhodizonate reaction was observed.

n it; but up to the present I have not been able actually to determine the substance or substances contained in this oxidation product.

In connection with these experiments, trials with other oxidising agents, such as aqueous bromine in presence of iron and platinum, are being made, which promise to yield results. The action of an ammoniacal solution of silver carbonate has also been investigated. A solution of 5 grams of inosite in dilute nitric acid was heated to boiling in a retort, and moist silver carbonate was added at intervals. The silver was thus freely reduced and ammonium carbonate appeared in the neck of the retort. On further reduction of silver took place, the operation was repeated, the liquid filtered off and evaporated. The silver residue, on the other hand, was extracted with dilute hydrochloric acid, and the acid liquid evaporated on a water-bath. The residue yielded a small quantity of ammonium oxalate, whilst from the mother liquor nothing but oxalic acid was obtained. As this result indicates that the reaction had been carried too far, the experiment was repeated with a less amount of silver carbonate. But also, although some unchanged inosite was recovered, no substance besides oxalic acid could be found.

In conclusion, I beg to offer my thanks to the managers of the Faraday Laboratory for having afforded me the opportunity to carry out these investigations.

FARADAY LABORATORY,  
ROYAL INSTITUTION.

#### XVIII.—*Hydrates of Some Quaternary Bases.*

By DAVID COWAN CRICHTON (Carnegie Research Scholar).

AND JOHNSTON (Trans., 1905, 87, 955) have described a method for preparing tetramethylammonium hydroxide by the interaction of potassium hydroxide and tetramethylammonium chloride in solution, and have shown how definite hydrates of the quaternary base may be separated from the solution obtained. At Mr. Johnston's suggestion I have prepared by the same method solutions of tetraethylammonium and tetrapropylammonium hydroxides, dimethylsulphine hydroxide, and in this paper hydrates of the quaternary bases are described.



*Tetraethylammonium Hydroxide*

The preparation of this base was conducted as follows: of potassium hydroxide, dissolved in eight times its weight alcohol, were mixed with 33.9 grams, the equivalent of tetraethylammonium chloride dissolved in its own weight alcohol. A bulky precipitate of potassium chloride at once and was removed after an hour's interval by filtration through an asbestos filter, the operation being carried out as rapidly as the aid of the pump in an atmosphere free from carbon dioxide. The filtrate was transferred to a large distilling flask and to it 100 c.c. of water. The methyl alcohol and a portion of the water were then removed under diminished pressure at a temperature exceeding  $50^{\circ}$ . When the distillation had continued for 12 hours the liquid, which then contained 44 per cent. of anhydrous base, was placed in a vacuum desiccator charged with phosphorus pentoxide. In the course of a few days, the liquid partly set to a mass of needles, which were separated by filtration on an asbestos filter and preserved in a closed glass-box in a desiccator. A second crop of the hydrate was prepared in a similar way, 47.5 grams of base in all being obtained from 70 grams of the chloride.

The crystals were proved to be free from potassium chloride, and titration showed them to contain four molecules of crystallisation.

I.	0.2442	required 44.1 c.c. of $N/40$ HCl.	Equiv. = 221
II.	0.1563	" 27.3 " "	226
III.	0.1050	" 19.4 " "	221

$N(C_2H_5)_4OH, 4H_2O$  has the equivalent 219.

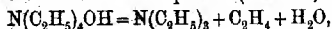
Analysis of the crystals dried in a vacuum resulted as follows:

I.	0.1472	gave 7.76 c.c. of nitrogen at N.T.P.	$N = 6.6$
II.	0.2014	" 10.84 " "	$N = 6.7$
III.	0.3957	" 0.5823 $CO_2$ and 0.4343 $H_2O$ .	$C = 44.14$ ;
IV.	0.1612	" 0.2612 $CO_2$ " 0.1915 $H_2O$ .	$C = 44.19$ ;
$N(C_2H_5)_4OH, 4H_2O$ requires $C = 43.84$ ; $H = 13.25$ ; $N = 6.3$			

A tetrahydrate of tetraethylammonium hydroxide thus obtained from aqueous solution instead of a pentahydrate as is the tetramethylammonium hydroxide under the same conditions.

Tubes containing small weighed quantities of the tetrahydrate, preserved over phosphorus pentoxide at various temperatures and pressures in order to ascertain if it were possible to dehydrate wholly or partly. At the ordinary temperature and pressures the loss of weight is very slow, but in an evacuated space the dehydration proceeds with considerable rapidity. Thus 0.2276 g

desiccator was found to have lost 0.046 gram in three days, however, was not due to dehydration alone, for the solution titration was found to possess the equivalent 217, which is slightly the equivalent of the tetrahydrate. Another sample 0.1169 gram, lost 0.0224 gram in two days at 15° in a desiccator, and was obtained by means of a mercury pump. The residue on reweighing had the equivalent weight of 220. It is apparent from these results that the tetrahydrate when it loses water also loses ammonia at the ordinary temperature, as the hydroxide is volatile. As the decomposition observed by Hofmann is in the sense of the equation (*Annalen*, 1851, 78, 268):



the contents of one of the tubes (originally evacuated by a Krafft mercury pump) were collected by the aid of a vacuum pump, and were found on analysis to consist of practically pure triethylamine. It is thus impossible directly to dehydrate the tetraethylammonium hydroxide at or above the ordinary temperature without the base itself undergoing decomposition. This is in sharp contrast to that of tetramethylammonium hydroxide which can be dehydrated to the stage of monohydrate without decomposition sets in (Walker and Johnston, *loc. cit.*, p. 960). The salts of tetrahydrate are extremely soluble in water, disengage a considerable absorption of heat. They melt at 49–50° without perceptible decomposition.

Comparative strength of the base as against sodium hydroxide was determined in *N*/100 solution by the rate of saponification of methyl acetate, using Walker's conductivity method (*Proc. Roy. Soc.*, 1901, 1, 152). It was found that if the strength of sodium hydroxide in centinormal solution is represented by 100, that of tetraethylammonium hydroxide in equivalent solution is represented

by 14.35. *rate.*—The filtrate from the original preparation of tetraethylammonium hydroxide was found, when it had stood for some days in a desiccator, to have lost a further quantity of crystals, larger in size than those of the original crop. These were dried on porous porcelain and gave the following result:

Required 14.35 c.c. *N*/40 HCl. Equiv. = 260.

“ 29.4 “ “ 255.

$N(C_2H_5)_4OH \cdot 6H_2O$  has the equivalent 255.

The composition is that of a hexahydrate. When heated, the crystals melt at 50°. A portion which had been melted and solidified gave the following result on titration:

Required 35.0 c.c. *N*/40 HCl. Equiv. = 255.

The hexahydrate can thus be melted without fundamental change. At 55°, however, the liquid obtained by fusion of the hexahydrate begins to decompose, the odour of triethylamine being distinctly perceptible. When the liquid which has been heated for some time and then cooled, the solid obtained has the composition of the hexahydrate. The tetrahydrate may also be formed from the hexahydrate by dehydration in a vacuum over phosphorus pentoxide. One gram of hexahydrate lost 0.0154 gram in two days, and the weight of the residue was found to be 220, the equivalent of the tetrahydrate being 219. That the hexahydrate is converted to a lower hydrate is made evident by the progressive lowering of the melting point of the solid which results on cooling. Thus the hexahydrate which originally melted at 49.5° was found after being heated for five minutes to melt at 47°, and after thirty minutes' heating at 43°.

The hexahydrate, like the tetrahydrate, dissolves in water with a notable absorption of heat.

#### *Tetrapropylammonium Hydroxide.*

Tetrapropylammonium chloride was dissolved in methyl alcohol and mixed with the equivalent quantity of potassium hydroxide in the same solvent. An abundant precipitate of potassium chloride was at once separated. The subsequent treatment was identical with that described under the preparation of tetraethylammonium hydroxide. The aqueous solution finally obtained did not crystallise at 0° for a week in a vacuum desiccator over phosphorus pentoxide, even on prolonged exposure to a temperature of -20° and on solidification. A portion of this liquid, which had approximately the composition of a heptahydrate, was sealed in an evacuated tube over phosphorus pentoxide, and gently warmed for some time. In a freezing mixture, the liquid now partly crystallised, the crystals disappeared when the temperature rose to that of the freezing mixture. However, by rapid filtration through an asbestos filter in a good freezing mixture, it was found possible to separate the crystals from the mother-liquor. The crystals melted at the room temperature and the liquid formed by their fusion was found to contain potassium chloride. Making allowance for this impurity, it was ascertained that 0.315 gram of the hydroxide required 0.140 N/40 HCl for neutralisation, corresponding to an equivalent weight of 329. The heptahydrate of tetrapropylammonium hydroxide has an equivalent weight of 329, so that in all probability the crystals consist of the heptahydrate. The liquid from which the crystals separated was the

same composition. Attempts to prepare a lower hydration were unsuccessful.

*Trimethylsulphine Hydroxide.*

A solution of trimethylsulphine hydroxide was prepared from sulphine chloride and potassium hydroxide according to the method readily described, except that the temperature at which it was conducted did not exceed 40°. The solution had approximately the composition of an octahydrate, and would not crystallise in a freezing mixture, and even after standing in a vacuum tube over phosphorus pentoxide showed no crystallisation at -20°, although it then had a composition between that of a pentahydrate and a tetrahydrate. Attempts at dehydration and crystallisation were unsuccessful, the base decomposed.

COLLEGE,  
EE.

### XIX.—*para-Toluidine Monohydrate.*

ALGER K. ALKER and HEATHER HENDERSON BEVERIDGE (Carnegie Research Scholar).

In the course of an investigation on the conductivity of the salts of *p*-toluidine it was found necessary for comparison to determine the conductivity of *p*-toluidine hydrochloride. We were surprised to find that the results obtained by the method in which the solution was prepared, did not agree with those obtained by Bredig (*Zeitsch.*, 1894, 13, 323). When, on the other hand, the base was recrystallised from aqueous alcohol and a weighed amount of standard hydrochloric acid, the results were much higher, corresponding to a deficit of about 10% of the base, or a like excess of acid. Since the concentration of the acid was correct, it was necessarily the *p*-toluidine which was in deficit, although the melting point of the sample used was optically that given in the ordinary works of reference. The anomaly could be most readily explained by the assumption that *p*-toluidine monohydrate crystallises from aqueous alcohol in the form of a hydrate. No mention of a hydrate is made in Beilstein's *Handbuch*, but the existence of a hydrated form of the base had been suggested by Lewy (*Ber.*, 1886, 19, 2728), who, however, did not

pursue the subject further, but merely stated that the crystals from aqueous solution effloresced when exposed to the air.

That the base crystallised from aqueous alcohol as a solid was seen on heating the dry crystals in a test-tube. As the temperature approached  $40^{\circ}$ , a film of moisture formed on the cold test-tube, and when the melting point was reached the liquid was plainly not homogeneous, globules of water being apparent in the fluid.

The conductivity numbers indicated that the substance was approximately the composition of a monohydrate, but some trouble was experienced in obtaining a sample suitable for account of the readiness with which the hydrate effloresced water in a desiccator, or even when exposed to the air under ordinary conditions. By adopting the following device, however, general applicability in the preparation of hydrates, we were able to obtain specimens with a constant amount of water. When small moist crystals of the hydrate were exposed in a desiccator to the action of a large quantity of the anhydrous base, with a dehydrating agent. The anhydrous substance is in equilibrium with the pressure of water vapour afforded by the lowest hydrate which can absorb water from any substance which has a higher vapour pressure than this. Consequently the adherent moisture is completely removed by the anhydrous base, but the water of hydration of the hydrate (in the present case the monohydrate) remains. In general terms, a hydrate can be completely dried, without being decomposed, by the dehydrating action of the next lower hydrate of all being prepared by the dehydrating action of the anhydrous substance.

A sample of the substance dried in this way lost not more than 1 per cent. of its weight after twenty-four hours' exposure, but on comparison over calcium chloride and solid potassium hydroxide it lost 10 per cent. of its weight. In carrying out the complete quantitative analysis, it is necessary to strew the desiccator with finely-divided *p*-toluidine in order that there may be no loss of the weighed quantity by vaporisation of the *p*-toluidine which is carried off. The loss actually found corresponded closely with that calculated from the formula of a monohydrate,  $C_7H_9N \cdot H_2O$ , namely, 14.4 per cent.

Elementary analysis confirmed this result:

0.1502	gave	0.3700 $CO_2$	and	0.1210 $H_2O$ .	$C = 67.10$ ;	$H = 12.65$
0.1265	"	0.3105 $CO_2$	"	0.1025 $H_2O$ .	$C = 66.94$ ;	$H = 12.275$
0.2275	"	22.1 c.c. moist nitrogen	at	$15^{\circ}$ and 771 mm.		
0.2089	"	19.1 c.c. "	"	12.5° "	776 mm.	

$C_7H_9N \cdot H_2O$  requires  $C = 67.20$ ;  $H = 8.80$ ;  $N = 11.20$

then, which crystallises from a solution of *p*-toluidine aqueous alcohol at the ordinary temperature contains water. It does not differ greatly in appearance from substance as crystallised from a non-aqueous solvent, hence in behaviour on melting, when the operation is usual in a capillary tube, at all striking. The melting pure anhydrous base, as determined by the ordinary  $5^{\circ}$ ; when heated slowly, the hydrate shows signs of  $38^{\circ}$ , but does not properly melt until  $42.5^{\circ}$  is reached. A tube containing the anhydrous base is plunged into here is incipient liquefaction on the upper portion of the tube, but the bulk of the substance does not melt; on the other hand, melts completely under the same. In presence of water, the hydrate melts at a little below. Difference in behaviour of *p*-toluidine hydrate when heated in a closed capillary is no doubt due to the loss in the water of hydration as the heating progresses. In the ordinary atmosphere, the hydrate loses its water of crystallisation depending on the surface exposed and on the fineness of the crystals. The anhydrous base, on the other hand, is slowly converted to the hydrate when exposed to an atmosphere saturated with water vapour. The spontaneous dehydration of the hydrate may be observed under the polarising microscope. If a drop of aqueous solution is allowed to evaporate on the slide, the small crystals of the hydrate may be seen to break up into numerous small crystals of the anhydrous base, the bulk of the larger hydrate crystals remaining unchanged. The action of the *p*-toluidine itself destroys it.

Measurements of the vapour pressure of the hydrate at various temperatures was made in a Bremer-Frowein tensimeter. Over the hydrate is almost entirely due to water vapour, the vapour pressure of *p*-toluidine at its melting point does not differ from that of mercury. For convenience of manipulation, the tensimeter was provided with a stop-cock on a bridge between the bulb and the gauge, and the vertical tubes from the bulbs were not furnished with stoppers. Values for copper sulphate were obtained with this tensimeter which approximate those given by Frowein (*Zeitsch. physikal. Chem.*, 1887, 11, 1). One of the bulbs was charged with a mixture of anhydrous *p*-toluidine monohydrate, and the other was charged with phosphorus pentoxide. For low temperatures, bromonaphthalene was used in the gauge, and for higher temperatures mercury. The pressures, expressed in millimetres of mercury, are given in the sub-

*Vapour Pressure of p-Toluidine Monohydrate*

Temperature ...	5°	11°	18°	20°	25°	28°	30°	32°
Pressure.....	3.0	5.0	9.0	10.5	15.7	20.0	22.5	26.5

Vapour pressure of water	6.5	9.8	15.4	17.4	23.5	28.1	31.5	35.3
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It is somewhat remarkable, in view of these values for the pressure of the hydrate, that the substance should be efflorescent under ordinary laboratory conditions, for, in general, the pressure of the vapour in the atmosphere is greater than the vapour pressure of the hydrate. A special experiment showed that the hydrate lost weight when the pressure of water-vapour in the atmosphere was 8 mm. and the pressure registered in the tensimeter 6 mm. Under these conditions, the percentage of water in the hydrate solid had sunk from 14 to 8. Possibly this abnormality is due to the volatility of the base itself, although it was found that the weight of the anhydride when exposed to the air is much less than the loss of weight of the hydrate under the same conditions.

The vapour pressures registered for *p*-toluidine monohydrate are about 10 per cent. greater than those found by Frowd (p. 14) for zinc sulphate heptahydrate. In order to ascertain the behaviour of *p*-toluidine hydrate corresponded with the behaviour of zinc sulphate hydrate, a portion of the pure hydrate was enclosed in a glass vessel with a weighed quantity of zinc sulphate crystals having the composition  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ . It was found that the *p*-toluidine hydrate very slowly lost weight, and that the hydrated zinc sulphate experienced a corresponding gain. The behaviour of these two substances in the presence of each other is therefore in accordance with the behaviour of the vapour pressure derived from the tensimeter experiments.

Dilatometric observations were made for the purpose of ascertaining if any definite temperature of transition existed below the melting point of the hydrate. The dilatometer used was of the open type, but for convenience in filling and handling, the stem was bent into U-form close to the bulb. The dilatometer was charged with the solid hydrate and the bulb then filled with an aqueous solution of the base. Readings were taken, at intervals of a few degrees, from 4° up to the melting point, but no definite expansion was observed. Similarly, on cooling from the melting point to the ordinary temperature, the predicted contraction with fall of temperature was perfectly registered. From these experiments, it would appear, therefore, that in presence of the hydrate is stable up to the point at which it passes into

toluidine in water and a saturated solution of water in base. In this case, it was to be expected that anhydrous *p*-toluidine with water to form the hydrate at all temperatures up to the melting point of the hydrate. To test this conclusion, a flask charged with anhydrous *p*-toluidine and rapidly filled with a saturated solution of the base, the whole apparatus during the experiment being immersed in a thermostat at 41.0°. After the two solutions came into contact, contraction at once occurred and continued for about an hour. As the temperature throughout the experiment remained constant, and since a special experiment showed that no change in solubility could be detected when solutions were brought to the saturation point by anhydride and hydrate, the contraction could only be attributed to the process of hydration. When the temperature was raised to 41.7°, the hydrate expanded with a corresponding expansion in the dilatometer. At the melting point, then, the anhydride unites with water to form the hydrate.

When a finely-divided anhydrous base is brought into contact with an aqueous solution of *p*-toluidine in a calorimeter, a rise in temperature is observed extending over about an hour, the heat of hydration being approximately 20 calories per gram of base. The assumption that the heat of hydration is constant, it is possible to use the laws of van't Hoff's formula:

$$Q = \frac{4.6}{T_1 - T_2} T_1 T_2 \log_{10} \frac{r_1}{r_2}$$

where  $Q$  is the heat of hydration, from the ratio,  $r$ , of the dissociation of water over the hydrate to the vapour pressure of the same temperature. The result of this calculation for the heat of hydration equal to about 29 cal. per gram of base. This value is greater than that found directly, but in view of the fact that the base became hydrated very slowly, the vapour pressures over the hydrate are not those of water and the approximation may be deemed sufficient.

This was made by Walker (*Zeitsch. physikal. Chem.*, 1890, 4, 100), who gave the heat of fusion of *p*-toluidine from the angle at which the solubility curves of the solid and liquid intersect at the melting point. This led to the value 44.5 cal. per gram instead of the value directly determined. It was not then suspected that the heat of fusion of the solid substance actually determined was that of the anhydrous base, but in view of the results of the present paper, it is obviously the solubility of the hydrate that was measured. The calculation therefore should lead to an



approximate value for the heat of fusion of the hydrate be  $32 + 25 = 57$  cal. per gram of anhydrous base if we value for the heat of hydration. The calculated number by no means in close accordance with this value.

UNIVERSITY COLLEGE,  
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### CLXX.—The Production of Orcinol Derivatives Sodium Salt of Ethyl Acetoacetate by of Heat.

By JOHN NORMAN COLLIE and EDWIN RODNEY CHEYSTALK.

THE production, by means of a simple reaction, of benzene from fatty compounds is always of interest, and, as noticed that by the action of heat on a mixture of ethyl and sodium ethoxide a compound was formed which gave reaction with chloroform and sodium hydroxide, the substance was thought to be worth while investigating. That orcinol it from diacetylacetone, and dimethylpyrone in the present has already been noticed (J. N. Collie and W. S. Myers, 63, 122). The amount produced, however, is very small. Jordan (Trans., 1899, 75, 808) has also obtained orcinol from ethyl acetonedicarboxylate.

The preparation of the condensation product of ethyl is easily carried out by heating ethyl acetoacetate with sodium ethoxide to convert about one-third of it into the sodium salt. Amounts usually employed were 78 grams of ethyl acetoacetate and 4.6 grams of sodium dissolved in 50 c.c. of absolute alcohol. The mixture was then heated in a distilling flask, ethyl acetoacetate distilled over, and the residue in the flask became deep orange and viscous. After cooling, hydrochloric acid was added, with stirring, and the oil separated. The solid substance was washed with alcohol and dried. The yield of crude orcinol was usually between 7 and 8 grams. It was purified by reprecipitation from benzene, from which it separated in long, colourless needles melting at  $168-169^{\circ}$ . On analysis:

C = 63.0, 62.8, 63.1\*; H = 5.1, 5.2, 5.4\*.

$(C_8H_8O_3)_n$  requires C = 63.2; H = 5.2 per cent.

\* The authors wish to express their indebtedness to Miss E. K. I. analyses marked with an asterisk in this paper.

Point was determined by the depression of the benzene, the numbers 296° and 320 were obtained:

$C_{16}H_{16}O_8$  requires M. W. = 304

is soluble in sodium hydroxide with a bright yellow colour, however, becomes much less intense on warming; by adding to the solution, a yellow, amorphous substance of high density is precipitated. This substance is peculiarly sensitive to alkaline solutions, yielding a purple colour which disappears on excess of alkali or acid. When a solution of the substance in alcohol is added to acetic acid, or distilled water, or carbon dioxide, its colour is yellow; strong alkalis give a brown colour; but if any of the following substances be added to the alcoholic solution, namely, London tap water, sodium sodium bicarbonate, lime water, sodium acetate, or even a solution of sodium acetate and some acetic acid, then the purple colour is precipitated.

and  $C_{16}H_{16}O_8$  may be evaporated to dryness with the benzene, leaving the unchanged substance. When boiled with sodium hydride, no acetate is produced.

with nitric and sulphuric acids acts with great violence on the substance, but no nitro-derivative could be obtained.

When, however, it gives a crystalline bromo-derivative. The bromination was carried out in acetic acid solution; on the addition of water, a yellow, crystalline compound separated. This was washed with water in hot alcohol to which a few drops of hydrochloric acid were added; otherwise decomposition of the compound with the addition of free bromine ensues. It melts at 182.5° and on analysis gives the following numbers:

C = 55.4, 35.9; H = 3.1, 3.6, 3.0; Br = 44.6, 45.0.

Analysis requires C = 35.4; H = 2.8; Br = 44.2 per cent.

The compound  $C_{16}H_{16}O_8$  is boiled with barium hydroxide solution, barium acetate, and barium carbonate are formed. When, however, one gram was boiled for some time with excess of sodium hydroxide solution, and the resulting barium carbonate after decomposing with hydrochloric acid yielded 150 c.c. of carbon dioxide; this corresponds to two molecules of carbon dioxide per molecule of the compound  $C_{16}H_{16}O_8$ .

When 93 per cent. sulphuric acid was next tried. Five grams of the substance were mixed with 10 c.c. of the acid and heated. On heating, effervescence of carbon dioxide began, and at 140° a large volume of gas occurred, the temperature being finally raised to 180°. The original substance dissolved in the sulphuric acid with a yellow colour which soon disappeared when the mixture was

heated. The products of the reaction were poured resulting precipitate being collected, washed with water further small amount was obtained by neutralising with solid sodium carbonate.

In another experiment, the amount of carbon dioxide measured; one gram yielded 78 c.c. of carbon dioxide corresponds to the evolution of one molecule of carbon dioxide of the compound  $C_{16}H_{16}O_6$ . The solid product crystallised from alcohol in small, colourless needles,  $250^\circ$  and contain water of crystallisation. On analysis

$H_2O = 8.3\%, 8.5\%, 8.7\%$ .

$C_{11}H_{10}O_8 \cdot H_2O$  requires  $H_2O = 8.6$  per cent  
 $C = 69.2, 69.0, 69.2$ ;  $H = 5.4, 5.6, 5.4$ .

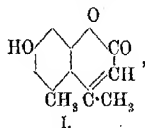
$C_{11}H_{10}O_8$  requires  $C = 69.2$ ;  $H = 5.4$  per cent

A molecular weight determination was made by the boiling point of an alcoholic solution:

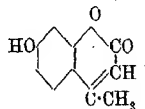
Found: M.W. = 196, 196, and 197.

$C_{11}H_{10}O_8$  requires M.W. = 190.

Finally, the compound was identified with dimethyl, obtained by the condensation of orcinol with ethyl acetoacetate von Pechmann and Cohen (*Ber.*, 1884, 17, 2188). These given the following formula to the compound:



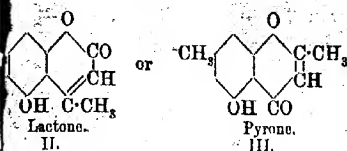
but did not prove the constitution of the substance, ... it from the constitution of condensation products of ethyl with other phenols. One of these, namely, the condensation of resorcinol with ethyl acetoacetate, has been undoubtedly has the constitution:



but its reactions are somewhat different.

Reagent.	Resorcinol Compound.	Orcinol
Sulphuric acid	Blue fluorescence.	No flu
Sodium hydroxide.	Faintly yellow solution, blue fluorescence.	Intense ; no fl

ate might, however, condense with orcinol differently,



ound possesses the lactone formula was easily proved it forms salts with bases. Two grams were boiled in sodium hydroxide solution, using a large amount of water, and barium was precipitated by carbon dioxide, and the residue, on cooling, a barium salt crystallised out. On analysis, it was found to contain Ba=25.0;  $(C_{11}H_{11}O_4)_2Ba$  requires 25.0 per cent.

had been a pyrone, no such compound would have

between the formula I, assigned to the compound by Cohen, and formula II was found to be more probable, as the compound behaves so differently from the one assigned to I, and when treated with either sodium hydroxide or sodium acetate, and also as it gives such an intense yellow colour with sodium acetate, it seems highly probable that formula II is the one which represents its molecular structure.

Experiments were tried to decide this point. The compound was treated with an excess of sodium ethoxide in the hope that perhaps a more volatile derivative might be formed, but only the unchanged substance could be separated from the products of the reaction. Sodium hydroxides dissolve the substance with a deep yellow color which mostly disappears on heating, but on the addition of acetic acid the original compound is reprecipitated. Even on fusion with sodium hydroxide at 180—200°, only the original substance and sodium carbonate could be separated from the products of the reaction.

On treatment with potassium permanganate took place at once in the presence of sulphuric acid could be detected in the oxidation products. The substance,  $C_{11}H_{10}O_3$  when heated with acetic anhydride gave a yellow solid of the acetate,  $C_{11}H_9O_3(C_2H_3O)$ ; it was recrystallised from benzene and melted at 198° (von Pechmann and Cohen give 195°).

$H = 5.6, 5.3$ .

$C_{12}O_4$  requires  $C = 67.2$ ;  $H = 5.2$  per cent.

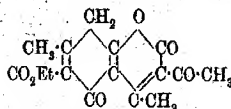
It was prepared by the action of methyl sulphate. It is a white, white needles melting at 146°. It is insoluble in water, except after prolonged boiling. On analysis:

$C_{11}H_{10}O_3$ ,  $H = 5.9$

$C_{11}H_{10}O_3$ ,  $OH$ , requires  $C = 70.6$ ,  $H = 5.9$

The oxidation of this compound by potassium also failed, but no oxidation products could be isolated. The action of hot sulphuric acid of about 93 per cent result in merely the removal of the methyl group, compound  $C_{10}H_{10}O_3$  was formed.

From the above reactions and decomposition of original compound  $C_{10}H_{10}O_3$ , a possible formula to it, namely:



It is not a true orcinol derivative until after sulphuric acid, and does not contain a hydroxyl group even, give a nitrogenous compound when treated with but as condensation also occurs in the alkaline solution formed was non-crystalline and could not be purified analysis.

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## CLXXI.—Derivatives of the Multiple Ket

By JOHN NORMAN COLLIE.

IN the present paper, the author wishes to call attention in which the group  $\cdot CH_2 \cdot CO \cdot$  (a group which he w "Kelen" group) can be made to yield by means of reactions a very large number of interesting compounds of interest being that these compounds be largely represented in plants.

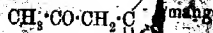
The syntheses of organic compounds in the laboratory know, are almost entirely different from those used in plants (compare Meldola, *Chemical Synthesis of Vital Products*, p. 7). Moreover, the photosyntheses which take place at present no parallel in the laboratory. Regarding the chief compounds in plants, the celluloses, the starches, sugars, at present we know but little.



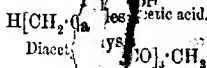
# COLLIE: DERIVATIVES OF THE

oxide, or of a ketene group, that the author proposes to call of the "multiple keten" group. For instance, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000

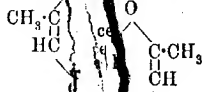
$\text{H}_2\text{CO}_3 \cdot \text{OH} - \text{H}_2\text{O} =$   
Tri-acetic acid.



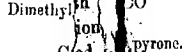
$[\text{CH}_2\text{CO}]_4 \cdot \text{OH} - \text{CO}_2 =$   
Tetra-acetic acid.



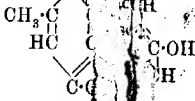
$[\text{CH}_2\text{CO}]_2 \cdot \text{CH}_3 - \text{H}_2\text{O} =$   
Diacetylacetone.



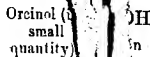
In acid solution.



$[\text{CH}_2\text{CO}]_2 \cdot \text{CH}_3 - \text{H}_2\text{O} =$   
Diacetylacetone.



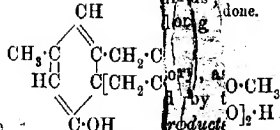
In strong alkaline solution.



$[\text{CO}]_3 \cdot \text{CH}_3 + \text{NH}_3 - 2\text{H}_2\text{O} =$   
Triaceton



$[\text{CO}]_3 \cdot \text{CH}_3 - \text{H}_2\text{O} =$   
lactone

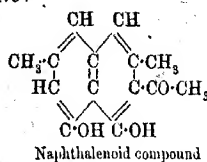


In faintly alkaline solution

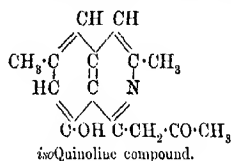
Benzenoid compound

enoid compound when dissolved in strong aqueous potassium

Sodium hydroxide loses another molecule of water, giving a benzene derivative:

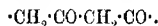


benzenoid compound when treated with ammonia at the ordinary temperature gives an isoquinoline derivative:



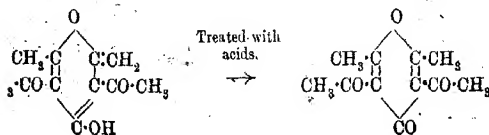
The ease with which all these condensations occur is most remarkable, as is also the diversity of the compounds produced.

The chief reason for the chemical reactivity of these compounds and why they often give quite different condensation products in alkaline solution is that they all possess the grouping the properties of which are well exemplified in ethyl acetoacetate, namely,

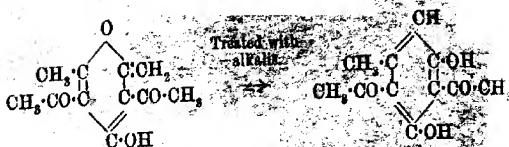


According to circumstances, this group may react either in the ketonic or enolic condition, and acids and alkalis are the reagents which are suited for bringing about this change in the molecular structure of the substance, a change which is usually expressed by a shifting in position of the double bond.

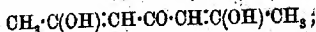
Amongst the derivatives of the multiple keten group, an interesting example is to be found in the compound obtained by the action of ethyl chloride on the sodium salt of diacetylacetone (Trans., 1904, 975). The substance is not a true pyrone derivative, neither is it a pyrazole compound, but hydrochloric acid converts it entirely into styldimethylpyrone, whilst sodium hydroxide transforms it into stylyrcinol.



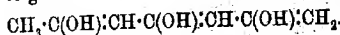




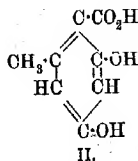
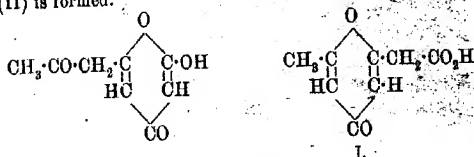
Several other instances might be given, for instance, diacetylacetone with acids gives dimethylpyrone, whilst with strong alkalis oreinol is formed in small quantity together with acetone and sodium acetate. The tendency of the acid is to produce:



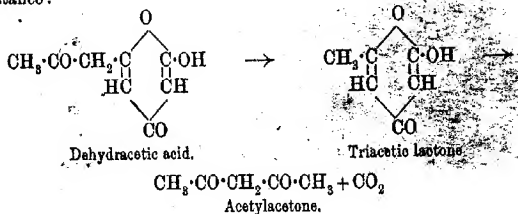
and of alkalis to give:



Dehydracetic acid also shows this difference. When sulphuric acid (Trans., 1907, 91, 787), it partly changes to a pyrom carboxylic acid (I), whilst with alkalis the isomeric oreinolcarboxylic acid (II) is formed.



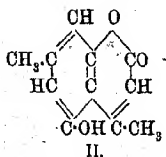
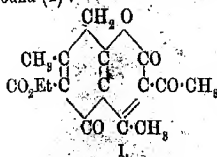
The chief action, however, of strong hydrating agents is to produce simpler substances. For instance, dehydracetic acid, diacetylacetone, dimethylpyrone, &c., give acetic acid and acetone when boiled with strong aqueous sodium hydroxide. But with different strengths of sulphuric acid, the down-grade hydrolysis can be better followed, for instance:



finally the acetylacetone breaks down into acetone and acetic

in the case where, however, there is a stable ring formation, such as the diacetylorninol mentioned above, strong hydrating agents merely split off the side keten groups and orninol is left.

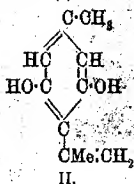
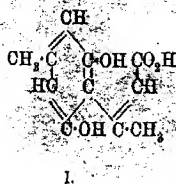
Another point of interest in these substances is the ease with which carbon dioxide is eliminated from them. The simplest case of this kind of course, acetoacetic acid. But dehydracetic acid also suffers this; when converted into tetra-acetic acid by hydrolysis. The isomeric monocarboxylic acid decomposes so easily that considerable loss occurs during crystallisation, the solution effervescing through loss of carbon dioxide. Orninolcarboxylic acid also is very unstable, easily losing carbon dioxide. It has already been shown how, from the combination of two molecules of diacetylacetone in concentrated or in slightly dilute solution, more complicated derivatives of the multiple keten group can be produced. This is found to be the case also when the sodium salt of ethyl acetoacetate is heated (see preceding paper); the compound  $C_{16}H_{16}O_8$  being partly a benzenoid and partly a pyrone compound (I):



has also been pointed out how, when this substance is hydrolysed with sulphuric acid, a simpler substance, dimethylumbelliferone (II), is produced.

The properties of this complex derivative (for the production of it from ethyl acetoacetate, only two simple reactions are needed) are of especial interest. Although colourless itself, with sodium hydroxide it gives a brilliant yellow compound. This is to be expected, for it is a "benzopyrone" compound, and therefore belongs to the same type as many of the yellow dyes.

Moreover, this brilliant yellow compound when warmed with more sodium hydroxide becomes nearly colourless, and the solution when acidified and extracted with ether gives the free acid (I):



This acid undergoes two interesting changes:

(1) On heating, it yields carbon dioxide and a substance (II) which has an odour resembling that of thymol; also when heated with phosphorus and iodine in a sealed tube traces of cymene are formed.

(2) When it is allowed to remain in a faintly alkaline solution in contact with air, the solution gradually absorbs oxygen, becoming a dark cherry-red. This is due to the formation of a dye which possesses properties similar to brazilin. The dye may be obtained from the acidified solution by extraction with ether, in which it is soluble. It then consists of a yellowish-red powder, but it could not be obtained pure owing to the fact that it could not be made to crystallise. Like brazilin, it dissolves in water with a yellow colour, which is at once changed to cherry-red by alkalis. It is decolorised by sodium hydroxide and zinc dust, but the colour is at once restored by shaking the colourless solution with air. Analysis gave:

C = 57.2; H = 4.5.

A molecular weight determination gave M.W. = 470.

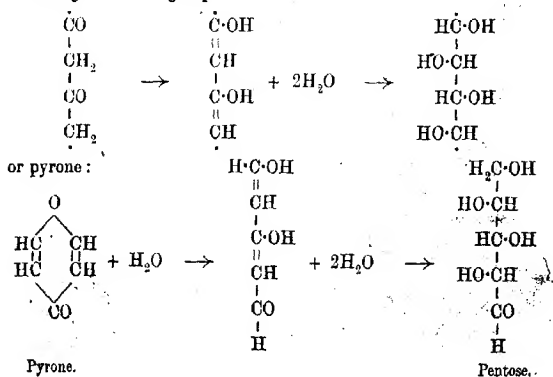
$C_{22}H_{22}O_{11}$  requires C = 57.3; H = 4.7 per cent. M.W. = 462.

Silk and cotton can only be dyed by this substance after mordanting; with alum, a brownish-red colour is produced.

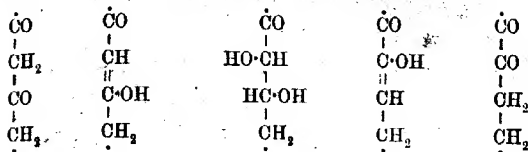
Whether the substance has a molecular structure similar to brazilin has not yet been ascertained, but it is not difficult to account for such a substance either on the lines of the formula of Kostanecki or that of Perkin.

In conclusion, the close relationship of these pyrone or keten compounds to the sugars, and through them to the starches and celluloses, might be pointed out. The whole question is one of hydrolysis.

Taking two keten groups:



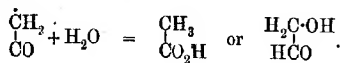
whilst if the hydration were to take place in another way :



then, in a long chain of keten groups, or hydrated keten groups (such as are undoubtedly present in the starches and celluloses), there would be an accumulation of oxygen towards one end of the chain, that is, carbon dioxide would be evolved; whilst at the other end, hydrogen or  $\cdot\text{CH}_2\cdot$  groups would predominate.

This might be offered as an explanation of the formation of fats and oils, and the production of carbon dioxide. That some such change can occur is plainly seen by the formation of alcohol, carbon dioxide, succinic acid, and glycerol from dextrose by fermentation. It is the living ferment that can effect this particular kind of hydrolysis.

Free keten reacting with water gives acetic acid, but perhaps under the influence of healthy protoplasm, glycollaldehyde and its polymerides might be produced :



It has already been pointed out by the author (Trans., 1905, 87, 48) that when  $\cdot\text{CH}_2\cdot$  groups are combined with carbon monoxide means of the silent electric discharge, combination occurs and a new group results. Moreover, that the  $\cdot\text{CH}_2\cdot$  group easily combines itself forming complex chains of  $\cdot\text{CH}_2\cdot$  groups was also noticed, but what was of considerable interest was the fact that certain definite nuclei of these  $\cdot\text{CH}_2\cdot$  groups appeared to be more stable than others. These nuclei are represented by  $\text{C}_{10}$  and  $\text{C}_{15}$  or  $\text{C}_{16}$ . Such nuclei are found in the terpenes and in the fatty acids.

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CLXXII.—*Racemisation by Alkali as Applied to the Resolution of *r*-Mandelic Acid into its Optically Active Isomerides.*

By ALEX. MCKENZIE and HERMANN AUGUST MÜLLER, Ph.D.

SOME three years ago, one of us (Trans., 1904, 85, 1249) attempted to effect the asymmetric synthesis of mandelic acid from benzoylformic acid by the aid of *l*-menthol, the method adopted being to reduce *l*-menthyl benzoylformate by aluminium amalgam, saponify the product, and then completely remove the menthol from the resulting mixture. It was anticipated at the time that an asymmetric synthesis would be brought about in accordance with the scheme:  $C_6H_5 \cdot CO \cdot CO_2H \rightarrow C_6H_5 \cdot CO \cdot CO_2 \cdot C_{10}H_{19} \rightarrow C_6H_5 \cdot CH(OH) \cdot CO_2 \cdot C_{10}H_{19} \rightarrow C_6H_5 \cdot CH(OH) \cdot CO_2H$ . The mandelic acid, obtained by this method, was, however, invariably optically inactive, although there was distinct evidence that the reduction of the benzoylformate had actually proceeded asymmetrically. That the reduction product in such a case is a mixture of unequal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate, containing a slight preponderance of the latter, was indicated by a determination of its specific rotation, which gave a value numerically higher than that of the partially racemic *l*-menthyl *r*-mandelate; the latter ester, which is readily formed from the *r*-acid, would have been produced if the reduction had proceeded symmetrically. The failure to realise the asymmetric synthesis of mandelic acid was found to be due to the racemising effect exercised by the alkali during the saponification of the ester mixture. It was noted in this connexion that partial racemisation takes place with remarkable ease when *l*-menthyl *l*-mandelate is saponified by alcoholic potassium hydroxide; *l*-mandelic acid is easily converted into this ester, but the *l*-acid cannot be regenerated from it free from the *r*-isomeride, no matter under what conditions the saponification is conducted. The behaviour of *l*-menthyl *d*-mandelate on saponification is similar.

Marckwald and McKenzie showed that, when *r*-mandelic acid is heated at 155° for one hour with *l*-menthol, the unesterified acid is levorotatory, and on this observation a method was based for resolving optically inactive compounds into their active components differing in principle from any of Pasteur's classical methods (*Ber.*, 1899, 32, 2130; 1900, 33, 208; 1901, 34, 469; Marckwald and Meth, *Ber.*, 1905, 38, 801). The conclusion was drawn that the velocity of formation of *l*-menthyl *d*-mandelate is greater than that of *l*-menthyl *l*-mandelate during the heating of the *r*-acid with *l*-menthol, and it

was found subsequently by direct measurements of the velocity of saponification of these esters that the *d*-mandelate is the more readily saponifiable of the two (McKenzie and Thompson, Trans., 1907, 91, 789). The fractional saponification of *l*-menthyl *r*-mandelate was also studied (Ber., 1899, 32, 2130; Trans., 1904, 85, 378). This ester is obtained by esterifying *r*-mandelic acid by *l*-menthol as completely as possible according to the Fischer-Speier method; it is a partially racemic ester, which is easily prepared in a state of uniformity, since under ordinary conditions it may be crystallised unchanged and is, accordingly, not resolved on crystallisation. When saponified by an excess of alkali, it yields the *r*-acid. When an insufficiency of alkali was used, the fractional saponification method of Marckwald and McKenzie gave, on almost every occasion, a dextrorotatory acid.

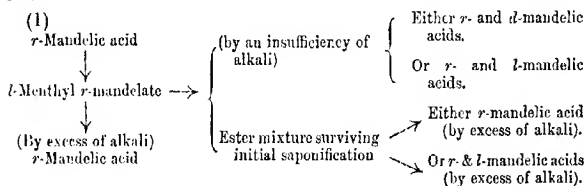
This result is normal. An alcoholic solution of the partially racemic ester contains equal amounts of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate. Since the former is the more readily saponifiable of the two, the fractional saponification of the partially racemic ester by alcoholic potassium hydroxide might be expected to give a dextrorotatory potassium salt. On two separate occasions, however, a levorotatory salt was obtained, and, at the time, the reason of this was not clear. The racemisation phenomena, however, subsequently observed during the saponification of menthyl and bornyl esters by alkali (McKenzie and Thompson, Trans., 1905, 87, 1004) threw light on this problem, and many unsuccessful attempts were accordingly made to obtain the conditions under which a levorotatory potassium salt would result on the fractional saponification of the partially racemic ester in question. These attempts have been continued with success, and the results are embodied in the present paper.

When the fractional saponification is conducted in concentrated solution under the conditions recorded in the experimental part, a levorotatory potassium salt is formed, and from this a specimen of the pure *l*-acid may be isolated. It is shown that, as a product of the fractional saponification of *l*-menthyl *r*-mandelate in alcoholic solution, either a dextrorotatory or a levorotatory acid may be obtained from the same weight of ester and using the same weight of alkali.

In each case, in addition to the fractional saponification, racemisation by alkali of the active potassium salt formed occurs. The formation of the dextrorotatory potassium salt is easily accounted for, the racemisation phenomena being in this case of secondary importance. The formation of the levorotatory salt, however, is due to the racemisation being pronounced, and is explained as follows. Shortly after the saponification has started, we have a mixture of (1) *l*-menthyl *l*-mandelate and *l*-menthyl *l*-mandelate, the latter being in excess; (2) potassium *r*-mandelate; (3) alkali; (4) ethyl alcohol, and (5)

menthol. If no racemisation had taken place, (2) would have consisted of a mixture of potassium *d*-mandelate and potassium *l*-mandelate with an excess of the former; the alkali is, however, strong enough at this stage to cause the formation of an inactive potassium salt. As the saponification proceeds, the concentration of the alkali becomes less and less, and its tendency to cause racemisation is also diminishing, until towards the end of the operation it is negligible. On the other hand, the ratio of *l*-menthyl *l*-mandelate to *l*-menthyl *d*-mandelate in the unsaponified portion is gradually increasing, so that the potassium salt formed, instead of being inactive as towards the start of the action, now becomes levorotatory. The explanation is simply that, in the initial stages of the saponification, the racemisation caused by the alkali is marked, and becomes less and less as the saponification proceeds. A similar interpretation had been previously advanced to account for the behaviour of *l*-menthyl *dl*-phenylethoxyacetate on fractional saponification (Trans., 1905, 87, 1004).

The following transformations, in which racemisation by alkali plays a part, have accordingly been realised:



(2) By conducting the fractional saponification of *l*-menthyl *r*-mandelate in such a manner that a dextrorotatory potassium salt is formed as the product of the initial saponification, and then saponifying the surviving ester mixture by an excess of alkali in such a manner that the racemising effect of alkali is brought into action, the change *r*-mandelic acid  $\longrightarrow$  *r*-mandelic acid and *d*-mandelic acid may be accomplished.

(3) By heating *r*-mandelic acid with *l*-menthol, removing the unesterified acid by shaking the ethereal solution of the reaction product with aqueous sodium carbonate, and then saponifying the residual ester mixture with an excess of alkali, the change *r*-mandelic acid  $\longrightarrow$  *r*-mandelic acid and *l*-mandelic acid may be brought about (Markwald and McKenzie, *loc. cit.*). This transformation can also be effected by conducting the fractional saponification of *l*-menthyl *r*-mandelate in such a manner that a levorotatory potassium salt is formed as the product of the initial saponification and then saponifying the surviving ester mixture by an excess of alkali. In the latter case, the racemising effect of alkali may or may not be caused to be pronounced.

It should be observed that these changes are not examples of asymmetric synthesis, inasmuch as the starting point is *r*-mandelic acid, a compound which already contains an asymmetric carbon atom.

Similar transformations may also be effected by aid of *l*-borneol. When *l*-bornyl *r*-mandelate is saponified by an insufficiency of potassium hydroxide, it generally gives a levorotatory potassium salt (Trans., 1904, 85, 378; 1905, 87, 1004) differing in this respect from *l*-menthyl *r*-mandelate and behaving abnormally, since *l*-bornyl *d*-mandelate is more quickly saponified than *l*-bornyl *l*-mandelate (Trans., 1907, 91, 789). It is, however, shown in the present paper that it is possible to choose such conditions that the racemising action of the alkali is minimised and a dextrorotatory potassium salt is formed. Accordingly, when *l*-bornyl *r*-mandelate is submitted to fractional saponification, either a dextrorotatory or a levorotatory potassium salt can be obtained at will.

#### EXPERIMENTAL.

*Change r-Mandelic Acid  $\rightarrow$  r-Mandelic Acid and l-Mandelic Acid.*

*l*-Menthyl *r*-mandelate was prepared as previously described (Trans., 1904, 85, 378). The ester (145 grams) was heated to melting at the temperature of a boiling-water bath, and 46.3 c.c. of ethyl-alcoholic potassium hydroxide (1 c.c. = 0.45 KOH), which is about three-fourths the amount necessary for complete saponification, were warmed and quickly added. The mixture was shaken vigorously, and the reaction was accompanied by a considerable development of heat. The product was heated at 100° under a reflux apparatus for five hours, but, since after twenty-four hours more at the ordinary temperature the liquid was still alkaline, the heating was continued for two hours longer, at the end of which time the liquid was neutral. The ethyl alcohol was then distilled off, an excess of water added to the residue, the precipitated ester mixture and menthol drained off, the filtrate extracted with ether, and the ethereal extract added to the ester mixture and menthol. The usual precautions were taken to ensure that the aqueous solution of potassium salt contained neither ester nor menthol, the solution having been evaporated to a small bulk and again extracted with ether, when no residue was obtained on removal of the ether. The aqueous solution of the potassium salt was acidified by mineral acid and extracted with ether (not quantitatively), when 33 grams of a mixture of *r*- and *l*-mandelic acids were obtained. A determination of the specific rotation of this acid mixture in ethyl alcohol gave the result:

$$l = 2, c = 10.57, \alpha_D^{14} = 1.15^\circ, [\alpha]_D^{14} = 5.4^\circ.$$

The mixture was then treated in the manner already described by



Marckwald and McKenzie (*Ber.*, 1899, 32, 2130) in order to separate a specimen of the pure *l*-acid. The bulk of the *r*-acid was first removed by crystallisation from water in such a manner that all the active acid remained in the mother liquors. The latter were then converted into magnesium salt, which was fractionated so that as much magnesium *r*-mandelate as possible was separated, the mother liquors again retaining the active product. On conversion of the latter into cadmium salt, a small amount of cadmium *r*-mandelate was removed, and the filtrate decomposed by hydrogen sulphide. In this manner, about 1.1 grams of nearly pure acid were obtained, which, on crystallisation from water, gave a specimen of the pure *l*-acid melting at 131.5–132.5°, and having the following rotation in aqueous solution:

$$l = 2, c = 0.9620, \alpha_D^{25} = -3.01^\circ, [\alpha]_D^{25} = -156.4^\circ.$$

The mixture of residual esters and menthol was freed from ether and the complete saponification carried out with a large excess of alkali in such a manner that the racemising action of the alkali was pronounced. The mixture was melted, and a warm solution of 80 grams of potassium hydroxide in 200 c.c. of ethyl alcohol was added quickly. After the vigorous reaction had subsided, the mixture was heated for two hours at the temperature of a boiling-water bath, and the subsequent manipulation conducted as before. The mandelic acid, obtained in this manner, was only slightly levorotatory, giving, in ethyl-alcoholic solution,  $\alpha_D = -0.14^\circ$  for a 10 per cent. solution in a 2-dm. tube.

Two other experiments may be quoted in order to show how an alteration of conditions affects the activity of the product from the final saponification. To the melted ester (9.7 grams) was added 2.7 c.c. of ethyl-alcoholic potassium hydroxide (1 c.c. = 0.112 KOH) and the mixture heated at 100° for one hour. The aqueous potassium salt, obtained in the usual manner, gave, on evaporation to the bulk, necessary to fill a 2-dm. tube, the value  $\alpha_D = -0.84^\circ$ , whilst the resulting mandelic acid mixture (1.5 grams) gave in ethyl-alcoholic solution:

$$l = 2, c = 10.24, \alpha_D^{18} = -0.81^\circ, [\alpha]_D^{18} = -4.0^\circ.$$

The residual ester mixture was then saponified by an excess of alkali, about five times more than was necessary. To the warm ester mixture was added 15 c.c. of ethyl-alcoholic potassium hydroxide (1 c.c. = 0.4536 KOH), but the subsequent heating at 100° was continued in this case for fifteen minutes only, with constant shaking. The mandelic acid mixture (3 grams), obtained in the usual manner, gave the following rotation in ethyl-alcoholic solution:

$$l = 2, c = 7.234, \alpha_D^{18} = -2.33^\circ, [\alpha]_D^{18} = -16.1^\circ.$$

$$l = 2, c = 10.15, \alpha_D^{19} = -3.25^\circ, [\alpha]_D^{19} = -16.0^\circ.$$

In another experiment, the same amount of ester was used as

Before, the same amount of alkali added under the same conditions, and the heating continued for four hours. The aqueous solution of potassium salt, when evaporated to the bulk necessary to fill a 2-dm. tube, gave in this case  $\alpha_D - 0.91^\circ$ , whilst the acid mixture gave in ethyl-alcoholic solution:

$$l = 2, c = 10.4, \alpha_D^{25} - 1.04^\circ, [\alpha]_D^{25} - 5.0^\circ.$$

The ester mixture was then saponified at the ordinary temperature and in dilute solution with slightly more than the calculated amount of alkali. The mixture of esters and menthol was dissolved in 100 c.c. of ethyl alcohol, and 50 c.c. of ethyl-alcoholic potassium hydroxide, containing 1.4 grams of alkali, was added, with constant stirring, during the space of two hours. After forty-eight hours, the solution was only slightly alkaline. The resulting mandelic acid mixture (3 grams) gave in ethyl-alcoholic solution:

$$l = 2, c = 5.21, \alpha_D^{25} - 1.25^\circ, [\alpha]_D^{25} - 12.0^\circ.$$

*The Change r-Mandelic Acid  $\rightarrow$  r-Mandelic Acid and d-Mandelic Acid.*

*l*-Menthyl *r*-mandelate (145 grams) was submitted to fractional saponification under conditions differing from those already given in the first experiment quoted in this paper. It is of importance to note that the weight of ester is the same as before, as also is the weight of alkali. The partially racemic ester was dissolved in 1500 c.c. of ethyl alcohol, and 500 c.c. of ethyl-alcoholic potassium hydroxide, containing 20.8 grams of alkali, was added, drop by drop, at the ordinary temperature within an interval of five hours, the solution being continuously stirred. In this manner, the racemising action of the alkali was reduced to a minimum. The solution was then allowed to remain for forty-eight hours at the ordinary temperature and was then neutral. The ethyl alcohol, unsaponified esters, and menthol were then removed as usual, and the aqueous solution of potassium salt, when decomposed by mineral acid, gave a mandelic acid mixture having the following rotation in ethyl-alcoholic solution:

$$l = 2, c = 10, \alpha_D^{25} + 0.76^\circ, [\alpha]_D^{25} + 3.8^\circ.$$

The yield of acid was 55 grams. The *r*-acid was removed in a manner similar to that already described for the isolation of the *l*-acid from the levorotatory acid mixture. Finally, 1.3 grams of nearly pure *d*-acid were obtained which, on crystallisation from water, gave a specimen of pure *d*-mandelic acid, melting at  $132-133^\circ$ , and showing the following rotation in aqueous solution:

$$l = 2, c = 1.065, \alpha_D^{25} + 3.29^\circ, [\alpha]_D^{25} + 154.4^\circ.$$

After the ether had been expelled from the solution of menthyl esters and menthol, which survived the initial saponification, the

product was completely saponified, using the same weight of alkali as in the first experiment quoted, namely, 80 grams. The resulting acid was slightly levorotatory, giving  $\alpha_D - 0.12^\circ$  for a 10 per cent. ethyl-alcoholic solution in a 2-dm. tube.

In the case of the final saponification, it is possible, by minimising the racemising effect of the alkali, to obtain an acid mixture with a specific rotation in aqueous solution as high as  $-15^\circ$ . In the example just quoted, the racemising action of the alkali was caused to be pronounced in order to make the change *r*-mandelic acid  $\rightarrow$  *r*-mandelic acid and *d*-mandelic acid more obvious.

*The Normal Fractional Saponification of l-Bornyl r-Mandelate.*

As has already been pointed out in the introduction, *l*-bornyl *r*-mandelate generally behaves abnormally on fractional saponification giving a levorotatory potassium salt, the residual ester mixture under the conditions formerly employed having given an inactive potassium salt. By varying the experimental conditions, a dextrorotatory acid mixture may be obtained from the initial saponification and a levorotatory acid mixture from the final saponification. Both saponifications were conducted at the ordinary temperature and in dilute solution.

Thirty grams of *l*-bornyl *r*-mandelate (Trans., 1905, 87, 1004) were dissolved in 1000 c.c. of ethyl alcohol and partially saponified by the addition, during the space of one hour, of 200 c.c. of ethyl-alcoholic potassium hydroxide; the amount of alkali in the latter solution was one-half of that necessary for complete saponification. The action was conducted with constant stirring at the ordinary temperature. After four hours at the ordinary temperature, the neutral solution was freed from ethyl alcohol, borneol, and residual esters, and gave a dextrorotatory acid mixture:

$$l = 2, c = 7.85, \alpha_D^{18} + 0.21^\circ, [\alpha]_D^{18} + 1.3^\circ \text{ (in ethyl-alcoholic solution).}$$

The mixture of residual esters and borneol was dissolved in 500 c.c. of ethyl alcohol and completely saponified by the addition, within the space of one hour, of 200 c.c. of ethyl-alcoholic potassium hydroxide containing slightly more than the calculated amount of alkali. After the solution had remained for twenty-four hours at the ordinary temperature, it was manipulated in the usual manner, the resulting mandelic acid being levorotatory:

$$l = 1.2, c = 9.98, \alpha_D^{18} - 0.99^\circ, [\alpha]_D^{18} - 5.0^\circ \text{ (in ethyl-alcoholic solution).}$$

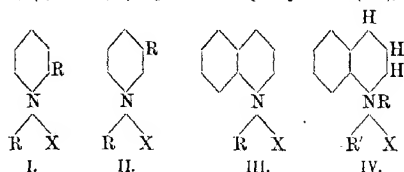
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### LXXIII.—The Optical Activity of Cyclic Ammonium Compounds.

By FRANK BUCKNEY, B.A., and HUMPHREY OWEN JONES.

It has now been clearly established in a large number of cases that a quinquivalent nitrogen atom of the type  $NabedX$  can give rise to optical activity due to the absence of a plane of symmetry in the molecule.

Certain compounds which contain a quinquivalent nitrogen atom forming part of a ring, as previously stated by one of us (*Trans.*, 1903, 83, 1405), contain no plane of symmetry, and so should be optically active. Accepting the current views as to the configuration of the nitrogen atom,  $\alpha$ - and  $\beta$ -substituted pyridinium compounds, (I) and (II), quinolinium compounds (III), and tetra-



hydroquinolinium compounds (IV) should all exist in optically active forms. Several compounds of the above type were prepared and their resolution attempted in the usual way, but without success (*loc. cit.*, 1415). Thus 1-methyl- $\alpha$ -picolinium *d*-camphorsulphonate and *d*-bromocamphorsulphonate, methylkairolinium-1-acetate *d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-methyl-1-ethyltetrahydroquinolinium *d*-bromocamphorsulphonate and 1-benzyl-1-ethyltetrahydroquinolinium *d*-camphorsulphonate were submitted to a long process of fractional crystallisation without separating them into the two constituents which were expected to be present.

Up to the present time, the only case in which the activity of a cyclic compound is attributed to a nitrogen atom is that of the ethylenedikairolinium salts examined by Wedekind (*Ber.*, 1905, 38, 1811). These salts, however, show certain abnormalities which have not yet been explained. Compounds in which activity is partly due to an asymmetric nitrogen atom have been prepared by Scholtz (*Ber.*, 1904, 37, 3627) from *d*-coniine.

It seemed desirable to make further attempts to obtain active cyclic compounds in which the activity was due to an asymmetric nitrogen atom, and, if possible, to throw some light on the difficulties which have hitherto prevented the resolution of such compounds.

The present paper contains an account of an examination of a number of compounds which, theoretically, should give rise to optical activity. Quinoline compounds could, in no case, be shown to exhibit activity, and in one case only could it be proved conclusively that a tetrahydroquinoline compound was optically active.

It is possible that in the quinoline compounds the existence of a double linking between the nitrogen and carbon atoms and the consequent possibility of oscillatory changes occurring at this point may prevent such compounds from exhibiting activity. At present, however, taking into account the quite exceptional difficulties which have been encountered in the resolution of tetrahydroquinoline derivatives, in which there can be no such effect, the evidence available is insufficient to justify the suggestion of possible explanations.

In all, eight tetrahydroquinoline derivatives of the necessary constitution,  $C_9H_{10}NRR_1X$ , have been examined, but in one case only, namely, that of the allylkairolinium salts, have we succeeded in obtaining conclusive evidence of optical activity due to the nitrogen atom.

It is at present impossible to understand what causes these compounds to be so much more difficult to resolve than other trivalent nitrogen compounds in which the nitrogen does not form part of a ring.

*Methylquinolinium d-camphorsulphonate* was prepared in the usual way from the corresponding iodide; after several recrystallisations from ethyl acetate, it melted at  $118^\circ$ , and gave values for the molecular rotatory power in aqueous solution of  $48.5-50^\circ$ , values approximating to that for the acid ion, namely,  $51.7^\circ$ .

*Benzylquinolinium iodide* was found to crystallise well and to melt at  $135^\circ$ . The *d-camphorsulphonate* was prepared and recrystallised from ethyl acetate nine times, when it was found to melt at  $120^\circ$  and gave  $[M]_D 48.4^\circ$ .

*Allylkairolinium iodide*\* was prepared and converted into the *d-bromocamphorsulphonate* in the usual way; this was found to be readily soluble in acetone and in ethyl acetate. After repeated recrystallisation from a mixture of acetone and toluene, the rotatory power of the less soluble fraction was found to diminish until it became constant, when  $[M]_D = 195^\circ$  approximately. The more soluble portion was purified by dissolving it in acetone, precipitating fractionally with light petroleum, and then evaporating the solution to dryness; in this way, the salt was obtained with  $[M]_D = 320^\circ$ . This was the *d*-base *d*-acid salt, but it was evidently impure.

It was observed that when the salt was allowed to separate slowly

\* A preliminary note on the activity of this compound has already appeared. Buckney, *Proc. Camb. Phil. Soc.*, 1907, 14, 177.)

in its solutions in ethyl acetate and toluene, two distinct kinds of crystals were deposited, one kind being short, transparent prisms, whilst the other consisted of long, silky needles. (This behaviour has been observed in other cases, notably that of phenylmethylallylpropylammonium *d*-camphorsulphonate, but the difference was found to be merely one of habit.) On separating these two kinds of crystals roughly by hand, a fairly simple process, it was found that the short prisms were the *l*-base *d*-acid salt, whilst the long needles were the *d*-base *d*-acid salt. Each sort of crystal was then recrystallised separately, when the *l*-base *d*-acid salt was obtained pure and the *d*-base *d*-acid salt fairly pure.

*l*-Allylkaironinium *d*-bromocamphorsulphonate.—The less soluble salt crystallises in small, colourless, transparent prisms melting at 164°:

0.1916 gave 0.3889 CO<sub>2</sub> and 0.1141 H<sub>2</sub>O. C = 55.4; H = 6.62.

C<sub>23</sub>H<sub>31</sub>O<sub>4</sub>NBrS requires C = 55.4; H = 6.43 per cent.

The following determinations of rotatory power were made on several samples, some of which had been purified simply by crystallisation and others by crystallisation after a rough mechanical separation:

0.109 in 11.81 of solution in a 2-dcm. tube gave  $\alpha_D$  0.75; hence  $[\alpha]_D$  40.6° and  $[M]_D$  202°.

0.133 in 12.03 solution in a 2-dcm. tube gave  $\alpha_D$  0.88°; hence  $[\alpha]_D$  39.8° and  $[M]_D$  198°.

0.161 in 17.12 of solution in a 2.2-dcm. tube gave  $[\alpha]_D$  0.81°; hence  $[\alpha]_D$  39.16° and  $[M]_D$  195°.

Taking the value of  $[M]_D$  for the acidic ion as 270°, we get  $[M]_D$  for the basic ion about -75° to -77°.

*d*-Allylkaironinium *d*-bromocamphorsulphonate was obtained fairly pure by recrystallising the long needles which had been separated mechanically, and consisted of long, silky needles melting at 153.5°:

0.1419 gave 0.2890 CO<sub>2</sub> and 0.855 H<sub>2</sub>O. C = 55.5; H = 6.69.

C<sub>23</sub>H<sub>33</sub>O<sub>4</sub>NBrS requires C = 55.4; H = 6.43 per cent.

The following determinations of rotatory power were made on different preparations:

0.1678 in 17.46 solution in a 2.2-dcm. tube gave  $\alpha_D$  1.46°; hence  $[\alpha]_D$  69.05° and  $[M]_D$  343.9°.

0.100 in 11.87 of solution in a 2-dcm. tube gave  $\alpha_D$  1.16°; hence  $[\alpha]_D$  68.8° and  $[M]_D$  342.9°.

Taking  $[M]_D$  270° for the acid ion, we get  $[M]_D$  +73.4° for the basic ion.

The iodide was not precipitated by the addition of concentrated potassium iodide solution to the solution used for the determination of rotatory power, but a small quantity of the crystalline iodide was deposited when a concentrated solution of the bromo-

camphorsulphonate was mixed with excess of concentrated potassium iodide solution. The quantity obtainable was not great enough to allow of trustworthy determinations of its rotatory power, which was also rendered the more difficult by the fact that the salt racemised very readily even in alcoholic solution. It was, however, observed that the solutions of iodides precipitated from the two different salts had opposite rotatory powers, and so proved that these salts contained the enantiomorphous bases. Thus 0.051 of the iodide precipitated from the less soluble bromocamphorsulphonate in 9.260 g. alcohol solution in a 2-dm. tube gave  $\alpha_D - 0.10^\circ$  ( $d = 0.800$ ); here  $[\alpha]_D - 11.3^\circ$  and  $[M]_D - 35.7^\circ$ .

The evidence detailed above leaves no room for doubt that the two forms of allylkairolinium salts have been separated and that both are optically active and enantiomorphously related to one another, and establishes the fact that an asymmetric nitrogen atom in a ring behaves normally.

Several other tetrahydroquinoline derivatives were examined and some of those already examined were re-investigated, but in no other case was any conclusive evidence of resolution obtained, although in several cases it will be seen that the values of  $[M]_D$  for the salts do not agree very closely with that for the acid ion.

*Benzylkairolinium d-camphorsulphonate* was prepared from the iodide and was found to be readily soluble in acetone or ethyl acetate; it was therefore recrystallised repeatedly from a mixture of ethyl acetate and toluene and finally melted at  $166-167^\circ$ .

The rotatory powers of successive fractions were determined, and  $[M]_D$  was found to vary from  $49.7^\circ$  to  $52^\circ$ , values almost identical with that for the acid ion, namely,  $51.7^\circ$ .

The iodide recovered from the camphorsulphonate was found to be quite inactive in alcoholic solution.

*Benzylkairolinium d-bromocamphorsulphonate* was prepared and recrystallised repeatedly from a mixture of ethyl acetate and toluene; it then melted at  $176^\circ$  and gave values of  $[M]_D$  varying from  $270^\circ$  to  $275^\circ$ . The iodide recovered from this salt also was inactive.

Since it has frequently been found that salts which cannot be resolved at the ordinary temperature, owing to the fact that they are partially racemic, can be resolved at a higher temperature which is above the transition point of the double salt, it was thought possible that this end might be achieved in this case in the same way. The salt was therefore recrystallised from ethyl acetate and acetone in a water-oven. The value of  $[M]_D$  was then found to be  $279^\circ$ .

It was also recrystallised from amyl acetate on a water-bath, and the value of  $[M]_D$  was then  $275^\circ$  to  $284^\circ$  for different specimens.

The iodide recovered from this salt was practically inactive, the latest rotation ever observed being  $0.03^\circ$  in alcohol.

It has been shown that these ammonium compounds can be resolved by means of tartaric acid (Miss Homer, *Proc. Camb. Phil. Soc.*, 1907, ii, 196), and this method has subsequently been found to succeed in some cases where the camphorsulphonic acids had failed; the acid tartrate was therefore prepared by treating a solution of the base, obtained by acting on the iodide dissolved in alcohol and water with silver oxide, with the calculated quantity of tartaric acid and evaporating to dryness. The tartrate did not crystallise well from any solvents that were tried, and was purified by dissolving in alcohol and adding ether gradually until a turbidity was produced when the crystalline salt separated on standing. After repeating this process several times, the iodide was recovered and examined, but again it did not show any appreciable rotatory power.

*Ethylkairolinium d-camphorsulphonate* [the corresponding *d*-bromocamphorsulphonate had been examined previously (*loc. cit.*, 1417)] was prepared and recrystallised repeatedly from a mixture of acetone and benzene. It then melted at  $70^\circ$  and gave values of  $[M]_D$  for successive fractions varying from  $47^\circ$  to  $52^\circ$ , so that no resolution had been effected.

*n-Propylkairolinium iodide* was prepared by heating kairoline and propyl iodide in molecular proportions in a sealed tube to  $100^\circ$  for some days, until the mixture had set to a solid mass; the iodide, which was readily soluble in alcohol, was recrystallised from a mixture of alcohol and ether, and was obtained in plates melting at  $132-133^\circ$ :

0.1423 gave 0.2562  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ .  $C = 49.0$ ;  $H = 6.18$ .

$\text{C}_{15}\text{H}_{29}\text{NI}$  requires  $C = 49.2$ ;  $H = 6.31$  per cent.

The *d*-camphorsulphonate and the *d*-bromocamphorsulphonate were found to be crystalline, but the former was found to be very difficult to recrystallise from all the solvents available, and has not yet been examined.

The *d*-bromocamphorsulphonate is rather sparingly soluble in acetone or ethyl acetate, even when hot; after repeated recrystallisation from these solvents, it melted at  $177-178^\circ$ , and gave values for  $[M]_D$  from  $286^\circ$  to  $290^\circ$ . It was also recrystallised from a mixture of alcohol and ethyl acetate, and was obtained in large, colourless, transparent prisms melting at  $178-179^\circ$ , and then gave  $[M]_D$   $277-290^\circ$ .

The iodide could not be recovered from solutions of the bromocamphorsulphonate.

The *platinichloride* was precipitated in beautiful, orange prisms, darkening at  $210^\circ$ , and melting with decomposition at  $216^\circ$ ; these



were, however, almost insoluble in all the organic solvents available and so the compound could not be examined for rotatory power.

It is therefore doubtful whether any resolution has been effected in this case; it is, however, probable that there has been no resolution since the propyl compound would probably have a rotatory power much the same order of magnitude as the allyl compound.

These experiments are being continued, and other suitable compounds are also under examination.

The expenses of this investigation have been largely met by grant from the Government Grant Committee of the Royal Society, to which the authors are glad to make this grateful acknowledgment.

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#### CLXXIV.—*Some Double Ferrocyanides of Calcium, Potassium, and Ammonium.*

By JAMES CAMPBELL BROWN, D.Sc.

IN some modern text-books, solutions of calcium salts are said to form a precipitate on addition of ammonium chloride and potassium ferrocyanide. It was thought desirable to ascertain the composition of this precipitate and the conditions of its formation, and the investigation has led to a revision of, and addition to, our knowledge of double ferrocyanides.

##### *Preparation of Potassium Calcium Ferrocyanide.*

The salt,  $K_2CaFeC_6N_6$ , was prepared by mixing cold concentrated solutions of potassium ferrocyanide and calcium chloride in molecular proportions. The precipitate was washed in cold water and dried at  $100^\circ$ .

*Analysis.*—A weighed amount of the dried salt was gently ignited in a porcelain dish, treated with *aqua regia*, and evaporated several times with the same agent. The acid solution was filtered from the blue precipitate, which was washed, and the washings added to the filtrate. The clear filtrate was heated to boiling and made alkaline with ammonia. The ferric hydroxide was collected, redissolved, and again precipitated in order to remove all the potash, the filtrates being added to the original filtrate. This solution was then heated to boiling, and the calcium precipitated as oxalate and weighed as  $CaO$ . The filtrate

On the calcium oxalate was evaporated to dryness, during which some on still retained was precipitated; the dried residue was ignited to remove ammonium salts, dissolved in water, and the potassium as estimated as platinichloride. This is a tedious method, and not trustworthy, except as applied to calcium, because some potassium cyanide is lost by ignition, and because it is difficult to wash out the potash from the blue precipitate which is formed by treatment with *aqua regia*.

In later experiments, another method was adopted. A weighed portion of the salt was boiled with water and an excess of lead chloride. This results in the quantitative precipitation of lead ferrocyanide, the calcium and potassium passing into solution as chlorides. The solution was cooled and filtered from lead ferrocyanide and excess of lead chloride. The lead in the filtrate was precipitated by hydrogen sulphide, and in the solution, which was free from lead, the calcium was precipitated as oxalate and the potassium as platinichloride in the usual way. It was necessary to carry out the decomposition in neutral aqueous solution, because the presence of acid caused the decomposition of some of the ferrocyanide:

Found, Ca = 11.92 and 12.33. K = 23.94.

$K_2CaFeC_6N_6$  requires C = 12.12; K = 23.68 per cent.

As a check, the iron was determined with a mean result of 17.15, theory requiring 16.97 per cent. The salt, dried in the air, and then at 100°, showed no loss of water of crystallisation, and further drying at 120° produced no loss of weight. This salt must therefore be anhydrous. Moissan (*Traité de Chim. Min.*, iv, 429) quotes Marchand (*J. Ch. Médic.*, 1844, 20, 558) as attributing three molecules of water of crystallisation to this salt. Several specimens have been prepared, however, and none has contained water of crystallisation. It is white when pure, becoming slightly cream-coloured on exposure to light, and consists of small, quadratic prisms.

#### *Preparation of Ammonium Calcium Ferrocyanide.*

By treatment of the potassium calcium salt with an equivalent quantity of ammonium chloride, the ammonium was not substituted for potassium at the ordinary temperature.

(a) Concentrated solutions of calcium chloride and potassium ferrocyanide were mixed in molecular proportions, and the precipitate collected; to the filtrate, a large excess of ammonium chloride solution was added and the precipitate collected, washed with cold water, and dried.

(b) The precipitate of the potassium calcium ferrocyanide was boiled with water, and a large excess of ammonium chloride added. The precipitate now obtained was washed well with cold water and dried at 100°. The two precipitates obtained by methods (a) and (b) were found to be of identical composition, and yielded on analysis a practically constant quantity of ammonia, provided that a sufficient excess of ammonium chloride was employed. The potassium remained in the soluble portion. Comparatively small quantities of the ammonium calcium salt are obtained by methods (a) and (b).

(c) The salt was also obtained in larger amount by first preparing pure ammonium ferrocyanide and precipitating it by calcium chloride. The salt thus obtained agreed in composition with the precipitates obtained by methods (a) and (b) just mentioned. This salt is white when pure and fresh, and consists of minute, anhydrous, prismatic crystals. It becomes coloured by the action of light.

*Analysis.*—Ammonia was estimated by distilling a weighed portion of the salt with excess of potassium hydroxide, collecting the ammonia in standard sulphuric acid, and determining the excess of acid by standard sodium hydroxide, using litmus as indicator.

Analysis of the precipitate (a) and (b):

Found,  $\text{NH}_4 = 12.33$ ;  $\text{Ca} = 14.03$ .

Analysis of precipitate (c):

Found,  $\text{NH}_4 = 11.79$  and  $12.11$ . Mean =  $11.95$ .

$\text{Ca} = 13.45$  and  $14.01$ . Mean =  $13.73$ .

$(\text{NH}_4)_2\text{Ca}_2\text{FeC}_6\text{N}_6$  requires  $\text{NH}_4 = 12.5$ ;  $\text{Ca} = 13.89$  per cent.

The salt loses no water of crystallisation either at 100° or at 120°; it is therefore anhydrous.

*Determination of the Solubilities of Potassium Calcium Ferrocyanide and of Ammonium Calcium Ferrocyanide.*

From 2 to 3 grams of the dry salt in each case were added to 500 c.c. of distilled water in a flask and agitated for about thirty-five hours by bubbling washed air through the mixture at a temperature of 15–17°. The solution, which was of a yellow colour, was then filtered, and 100 c.c. of the clear filtrate were weighed and evaporated to dryness; the residue was dried at 100° and weighed. In each case, the result was checked by determining the amount of calcium as oxalate in 250 c.c. of the solution; from this, the amount of salt dissolved was calculated, the percentage of calcium in the salt being known.

*Potassium Calcium Ferrocyanide.*—One hundred c.c. weighed 100.04

grams and yielded 0.0475 gram of residuè. Consequently by evaporation it is found that:

100 c.c. dissolve .....	0.407 gram
By estimation of the calcium .....	0.412 „

Mean = 0.41 „

or 1 part of the salt dissolves in 244 parts of water at 15—17°.

*Ammonium Calcium Ferrocyanide.*—By evaporation it is found that:

100 c.c. dissolve .....	0.259 gram
By estimation of the calcium .....	0.257 „

Mean = 0.258 „

or 1 part of the salt dissolves in 388 parts of water at 15—17°.

As a qualitative test, it is manifestly desirable to form as much of the ammonium salt as possible, rather than the potassium salt; but under ordinary working conditions, the pure ammonium calcium ferrocyanide will not be the salt precipitated.

Experiments have shown that for each proportion of the reagents, potassium ferrocyanide, calcium chloride, and ammonium chloride, an equilibrium results, so that by greatly increasing the amounts of ammonium chloride the proportion of ammonium increases and the proportion of potassium decreases in the precipitated salt.

The following epitome of the results which have been obtained will bring out the principal points. The first four columns indicate the number of molecular proportions of the several salts which have been mixed, and column 5 shows the percentage of ammonium found in the precipitate.

*Precipitates formed from Concentrated Solutions.*

	1. Mol. $K_4FeC_6N_6$ .	2. Mols. $CaCl_2$ .	3. Mols. $AmCl$ .	4. Mols. $KCl$ .	5. % $NH_4$ .
1. ....	1	2	9	—	8.85
2. ....	1	1	1	—	3.90
3. ....	1	1	2	—	4.27
4. ....	1	1	6	—	8.17

*Precipitates formed from Dilute Solutions.*

5. Precipitated hot .....	1	1	1	—	2.54
6. „ cold .....	1	1	1	—	2.42
7. Precipitated by heating filtrate from 6 .....	1	1	1	—	2.46
8. ....	1	1	2	—	4.46
9. ....	1	1	6	—	8.43
9B. ....	1	1	6	—	8.42
9. ....	1	1	12	—	10.24
1. ....	1	1	20	—	11.29
1B. ....	1	1	20	—	11.27

$(NH_4)_2CaFeC_6N_6$  yields  $NH_4 = 12.5$  per cent.

*Effect of adding varying quantities of Potassium Chloride.*

	1. - Mol. $K_4FeC_6N_6$	2. Mol. $CaCl_2$	3. Mols. $AmCl.$	4. Mols. $KCl.$	% $NH_4$
12. ....	1	1	6	1	8.05
13. ....	1	1	6	2	7.41
14. ....	1	1	6	6	5.94

From experiments 5, 6, and 7, it is seen that the precipitate formed in the hot solution, that formed in the cold solution, and that formed on heating the filtrate from the cold solution are all practically identical. Experiments 12, 13, and 14, and many others, which it is needless to add to the epitome, show that by the presence of potassium chloride in the solution the amount of the ammonium present in the precipitated salt is decreased proportionally, but analyses of a number of the precipitates show that this is not due simply to substitution of potassium for ammonium and vice versa. The proportion of calcium is less than corresponds to  $Ca_2$ , and the salts are triple ferrocyanides of calcium, potassium, and ammonium.

In ordinary qualitative working, the best conditions for the test are to add approximately molecular proportions of potassium ferrocyanide to the calcium salt, a large excess of ammonium chloride, and to heat the mixture. A precipitate formed in this way from one molecular proportion each of calcium chloride and potassium ferrocyanide and six molecular proportions of ammonium chloride gave on analysis :

(I)  $Ca = 12.33$  ;  $K = 8.25$  ;  $NH_4 = 8.17$ . (II)  $Ca = 12.69$  ;  $K = 8.13$  per cent.

The figures in (I) would be given by a mixture containing 47.31 per cent. of calcium ferrocyanide, 19.46 per cent. of potassium ferrocyanide, and 32.23 per cent. of ammonia ferrocyanide.

A precipitate formed by mixing one molecular proportion each of calcium chloride and potassium ferrocyanide and twenty molecular proportions of ammonium chloride gave on analysis :

$Ca = 12.39$  ;  $NH_4 = 11.29$ , and a small proportion of potassium.

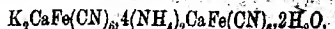
Here, ammonium has replaced some of the calcium as well as most of the potassium.

Precipitate No. 3 in the table, formed from one molecular proportion each of calcium chloride and potassium ferrocyanide and two molecular proportions of ammonium chloride, gave on analysis :

$C = 12.77$  ;  $K = 15.83$  ;  $NH_4 = 4.27$  per cent.

These figures would be given by a mixture containing 46.2 per cent of calcium ferrocyanide, 37.1 per cent. of potassium ferrocyanide, and 16.7 per cent. of ammonium ferrocyanide.

Since the above was written, it appears that F. B. Dains (*J. Amer. Chem. Soc.*, 1907, 29, 728) has attributed the formula:



to "the product formed by precipitating a calcium salt with potassium ferrocyanide in the presence of a large excess of ammonium chloride or nitrate." The proportions of the different substances mixed together are not stated, and the precipitates were dried at 70°.

No doubt analytical figures approximating to the percentages in this formula will be obtained from precipitates prepared within some limits, but by varying more widely the proportions of the several salts it becomes quite clear that the precipitate varies as the result of mass action.

If the figures given on p. 1830 as the result of mixing one molecular proportion each of calcium chloride, potassium ferrocyanide, and six molecular proportions of ammonium chloride had been calculated on the same principle as Dains' calculation, they would have indicated the formula:  $K_2CaFeC_6N_6, 2(NH_4)_2CaFeC_6N_6$ . The present author purposely refrained from writing such a formula, because a formula is apt to mislead the reader into thinking that the mixture is constant, which it is not.

The water shown in Dains' formula is obviously due to the salt having been dried at 70°.

By drying at a more appropriate temperature, the anhydrous character of the salt has been repeatedly confirmed.

I have to thank Mr. T. Callan, B.Sc., for his valuable assistance in carrying out the practical work and analyses.

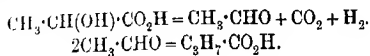
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# CLXXV.—*The Condensation of Acetaldehyde and its Relation to the Biochemical Synthesis of Fatty Acids.*

By HENRY STANLEY RAPER.

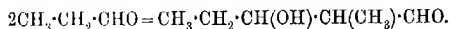
The formation of fatty acids in animals, from carbohydrates, and the occurrence in natural fats, such as butter, of all the fatty acids containing an even number of carbon atoms, from two to twenty, suggest that these fatty acids are produced by the condensation of some highly reactive substance containing two carbon atoms and formed in the decomposition of sugar.

It has been suggested by Nencki that in the butyric fermentation of lactic acid, acetaldehyde, carbon dioxide, and hydrogen are first formed, and that two molecules of the acetaldehyde then unite to form butyric acid:



Magnus Levy (*Englemann's Archiv*, 1902, 365) and Leathes (*Problems in Animal Metabolism*, London, 1906) have extended this suggestion to explain the formation of the higher fatty acids. Their conclusions receive support from the fact that *n*-hexoic acid has long been known to be a regular product of the butyric fermentation, and it has already been shown in a former communication (*Proc. Physiol. Soc.*, 1907, xxiv) that *n*-octoic acid is also produced to a small extent. According to the hypothesis referred to, therefore, in the formation of fatty acids from dextrose, lactic acid is the first product, and on the decomposition of this into acetaldehyde, carbon dioxide, and hydrogen, condensation of the aldehyde occurs, leading to the formation of the higher acids.

The chief difficulty in the acceptance of these views lies in the fact that all the previous work on the condensation of aliphatic aldehyde has shown that the products of condensation are aldehydes with branched, and not straight, chains (Lieben, *Monatsh.*, 1901, 22, 289). This is due to the tendency of the aldehyde group of one molecule to condense with the  $\alpha$ -carbon atom of the other molecule. Thus propionaldehyde on condensation gives rise to  $\beta$ -hydroxy- $\alpha$ -methylvaleraldehyde and not to hexaldehyde:

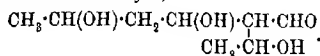


But it must not be forgotten that Lieben's deductions have been confined to observations made on the condensation of aldehydes, such as acetaldehyde, propionaldehyde, and valeraldehyde, which contain no hydroxyl groups; and, since when acetaldehyde condenses with itself the first product is necessarily  $\beta$ -hydroxybutyraldehyde (aldol), it is possible that the presence of the hydroxyl group in the  $\beta$ -position might influence the further course of the reaction, and conceivably lead to the production of an aldehyde with a straight chain.

The present paper deals with a study of this condensation, the first stage of which, namely, the formation of an aldehyde with eight carbon atoms from aldol, has been investigated. Previous observations on this subject are to be found in a paper by Wurtz (*Compt. rend.*, 1880, 91, 1030), in which a substance, dialdane,  $\text{C}_8\text{H}_{14}\text{O}_2$ , is described as a product of the condensation of acetaldehyde under the influence of hydrochloric acid. The substance is regarded as possessing the

constitution  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$ , but this formula is unsupported by evidence.

If the condensation of aldol followed the rule established by Lieben and his collaborators, then the first product of condensation should be  $\beta$ , $\beta$ -dihydroxy- $\alpha$ -ethanolhexaldehyde,



By condensation under the influence of dilute potassium carbonate aldol has been found to yield, not this substance, but a hydroxyoctaldehyde with a straight chain. Unfortunately, this aldehyde has never been obtained quite pure, and on this account a more complete examination of its structure has had to be abandoned. Analyses made with the substance purified as far as was possible indicate that on condensation a molecule of water is eliminated with the formation of an inner anhydride and not of an unsaturated compound as is generally the case. Under the action of traces of mineral acid, two molecules of the substance lose a molecule of water, forming an aldehyde,  $\text{C}_{16}\text{H}_{26}\text{O}_5$ .

That the carbon atoms are in a straight chain in the condensation product has been proved by oxidising it to the corresponding acid and then reducing this by means of hydriodic acid. In this way, *n*-octoic acid was obtained, and identified by means of its amide and barium salt.  $\alpha$ -Ethylhexoic acid, which would have been obtained at this stage had the condensation taken place according to Lieben's rule, has been prepared for comparison.

#### EXPERIMENTAL.

The aldol used in the experiments was prepared by the condensation of acetaldehyde in presence of 5 per cent. potassium carbonate solution (Orndorff and Newbury, *Monatsh.*, 1892, 13, 516).

*Condensation of Aldol.*—As condensing agent, a 5 per cent. solution of potassium carbonate was used. One hundred grams of freshly prepared aldol were mixed with 100 c.c. of distilled water and the solution cooled in ice. Five grams of solid potassium carbonate were then added in small portions, the solution being kept below  $10^\circ$  during the process. When the potassium carbonate had completely dissolved, the solution was kept at a temperature of  $13$ – $14^\circ$  until a yellow oil had separated at the bottom of the vessel. The time occupied was about sixty hours. The solution was now diluted to 800 c.c. with water, rendered slightly acid with hydrochloric acid, and the yellow, tarry substance separated. The filtrate was extracted with 200 c.c. of ether in order to separate a little of the tarry matter remaining in solution from the condensation product, which is much



less soluble. Barium carbonate was now added to the solution to neutralise the free acid, and the whole was distilled in steam for three hours to remove unchanged aldol. As the condensation product is also volatile to a small extent, a little is lost in this process. The solution in the distilling flask was now concentrated to a syrup by evaporating the water under reduced pressure, and extracted with ether. After drying the ethereal extract over anhydrous copper sulphate, the ether was removed by distillation and a pale yellow, very viscous liquid remained. The yield was 35 per cent. of the aldol taken.

The substance decomposed when distilled under the ordinary as well as under reduced pressure. It did not give crystalline derivatives by the usual methods applicable to aldehydes, although it gave the usual aldehyde reactions. On warming with a trace of calcium chloride or mineral acid, or on heating alone for some time, it gave rise to a new compound, which, unlike the parent substance, was less soluble in hot water than cold.

The molecular weight was determined by the boiling point method. For this purpose, the substance was heated to  $50^{\circ}$  under diminished pressure in a stream of dry carbon dioxide to remove the last traces of ether and moisture. The substance so obtained gave a slight opalescence on dissolving in water, which increased on warming:

0.7121 in 9.05 of alcohol raised the boiling point  $0.47^{\circ}$ . M.W. = 193.

0.7121 " 13.70 " " " "  $0.32^{\circ}$ . M.W. = 187.

$C_8H_{10}O_4$  requires M.W. = 176.  $C_8H_{14}O_3$  requires M.W. = 158.

On analysis:

0.1706 gave 0.3833  $CO_2$  and 0.1347  $H_2O$ . C = 61.28; H = 8.77.

$C_8H_{14}O_3$  requires C = 60.76; H = 8.86 per cent.

$C_8H_{16}O_4$  " " C = 54.54; H = 9.09 "

These analytical results indicate that a molecule of water is eliminated in the process of condensation.

The high value obtained for the molecular weight is due to the presence of a substance derived from two molecules of the aldehyde,  $C_8H_{14}O_3$ , by the removal of water. This change, as stated above, takes place very readily on warming with a trace of calcium chloride or mineral acid, or merely by heating alone for some time. The new substance thus formed is very easily recognised by being much less soluble in hot water than cold; its cold aqueous solution immediately becomes milky on warming. On analysis:

0.2091 gave 0.4973  $CO_2$  and 0.1607  $H_2O$ . C = 64.88; H = 8.54.

0.5250, in 7.37 of alcohol, gave an elevation of  $0.28^{\circ}$ . M.W. = 293.

0.5250 " 11.74 " " " "  $0.18^{\circ}$ . M.W. = 286.

$C_{10}H_{20}O_3$  requires C = 64.43; H = 8.72 per cent. M.W. = 298.

It was found impossible to obtain a specimen of the condensation product quite free from this anhydride, the mere heating in a vacuum in order to dry the substance for analysis causing a certain amount of hydration with consequent production of the anhydride. On this account, the analytical results can only be taken as approximately correct. When dissolved in acetic acid, the condensation product absorbed only a trace of bromine, so that it appears to be a saturated compound. It seems probable, therefore, that the water which is eliminated during condensation comes from two hydroxyl groups and thus gives rise to an inner anhydride.

#### *Oxidation of the Condensation Product.*

Freshly precipitated silver oxide in the presence of barium hydroxide was used as the oxidising agent. The silver oxide was obtained by precipitating silver nitrate with the requisite amount of barium hydroxide and washing until free from barium nitrate. It was not allowed to cake during the washing, as this materially affected the yield of acid.

Ten grams of the condensation product dissolved in 30 c.c. of water were added to 40 grams of freshly precipitated silver oxide suspended in about 400 c.c. of water. The mixture was cooled to  $10^{\circ}$ , and a solution of 10 grams of barium hydroxide in 200 c.c. of water added in portions of about 25 c.c. every five minutes. After each addition, the whole was well shaken and the temperature kept about  $10^{\circ}$ . When all the barium hydroxide had been added, the contents of the vessel were allowed to regain the room temperature. The shaking was continued at intervals of fifteen minutes for two hours. At the end of this time, the oxidation was usually complete. The silver and unchanged silver oxide were filtered off and well washed with distilled water, the filtrate and washings were mixed, and any excess of barium hydroxide precipitated by carbon dioxide. After filtering, the solution was distilled under reduced pressure until the residue became syrupy. This was dissolved in alcohol, filtered, if necessary, and the barium salt precipitated by the addition of ether. To remove any unchanged substance, the precipitate was re-dissolved in alcohol and again precipitated. The barium salt of the acid corresponding to the aldehyde,  $C_8H_{14}O_3$ , was thus obtained as a yellowish-white, amorphous, and very hygroscopic solid. It was dried at  $100^{\circ}$ :

0.2781 gave 0.1385  $BaSO_4$ . Ba = 29.30.

$(C_8H_{14}O_3)_2Ba$  requires Ba = 28.34 per cent.

The free acid was obtained by decomposing the barium salt with the calculated amount of sulphuric acid. On filtering off the barium sulphate, boiling with a little animal charcoal, again filtering, and

evaporating the filtrate under reduced pressure, the free acid was obtained as a very viscous liquid. The yield amounted to 70 per cent. The product did not crystallise even after standing for a considerable time in a vacuum over sulphuric acid. The lead, silver, calcium, and copper salts were prepared. The silver salt decomposed on drying. The lead, calcium, and copper salts were amorphous and very soluble, both in alcohol and water.

*Reduction of the Acid,  $C_8H_{14}O_4$ , with Hydriodic Acid.*

Ten grams of the free acid were boiled for five hours under a reflux condenser with 80 grams of hydriodic acid (b. p.  $127^\circ$ ) and 4 grams of red phosphorus. After cooling, the liquid was diluted with twice its volume of water and extracted several times with ether. The ethereal extract was shaken with mercury to remove free iodine and the ether then removed by distillation. A thick brown oil was left behind, which still contained combined iodine. To remove this, dilute sulphuric acid was added and then zinc dust in small portions. After standing for twenty-four hours, the volatile acids were removed by distillation in steam. The distillate was neutralised with sodium hydroxide and evaporated to dryness on the water-bath. The yield of sodium salts amounted to 20–25 per cent. of the acid taken for the reduction.

5.5 Grams of the sodium salts were decomposed with sulphuric acid, and the fatty acids thus liberated were extracted with ether and dried over anhydrous sodium sulphate. The ether was removed on the water-bath and the residual fatty acid distilled. 0.85 Gram of acid passed over at  $215$ – $233^\circ$ . Below  $215^\circ$ , a little butyric acid was obtained.\* The fraction boiling at  $215$ – $233^\circ$  was converted into the amide by Aschan's method (*Ber.*, 1898, **31**, 2348). After crystallising from light petroleum and then from water, the amide was obtained in glistening plates, which melted sharply at  $105$ – $106^\circ$ , corresponding with the melting point of *n*-octoamide. When mixed with pure *n*-octoamide, the melting point was unchanged.

From another portion of the acid, the barium salt was prepared by neutralising with barium hydroxide. It was crystallised twice from water in order to remove barium butyrate, and was obtained in colourless plates:

$C_8H_{14}O_4$  gave 0.0274  $BaSO_4$ .  $Ba = 32.55$ .

$(C_8H_{14}O_2)_2Ba$  requires  $Ba = 32.39$  per cent.

The acid obtained from the condensation product by oxidation and

\* This was due to the aldel not being completely removed from the condensation product by distillation in steam. In cases where the condensation product was not required for analysis, the steam distillation was shortened in order to lose as little as possible of the condensation product which is slightly volatile in steam.

reduction is therefore octoic acid; hence the first stage in the condensation of aldol results in the production of a hydroxyaldehyde with the carbon atoms united in a straight chain.

The residue, which did not distil at  $233^{\circ}$ , was converted into the barium salt and analysed:

0.1312 gave 0.0727  $\text{BaSO}_4$ . Ba = 32.61.

This was therefore barium octoate.

#### *Synthesis of $\alpha$ -Ethylhexoic Acid.*

This was carried out in the usual manner from ethylmalonic ester and butyl iodide. 1.7 Grams of sodium were dissolved in 20 c.c. of absolute alcohol and, after cooling, 14 grams of ethylmalonic ester added. 13.5 Grams of *n*-butyl iodide were now added, drop by drop, with frequent shaking. When all the butyl iodide had been run in, the mixture was heated on the water-bath for six hours, after which the alcohol was removed as completely as possible by distillation. The residue was dissolved in water, calcium chloride solution added, and the *ethylbutylmalonic ester* extracted with ether. After dehydrating the ethereal solution, the ether was removed on the water-bath and the ester distilled. Nine grams were obtained boiling at  $235\text{--}245^{\circ}$ . The ester was hydrolysed by boiling with the requisite amount of 30 per cent. aqueous potassium hydroxide. When hydrolysis was complete, the solution was extracted with ether to remove a little oily impurity, then acidified with dilute sulphuric acid, and the liberated acid extracted with ether. The ether was evaporated and the acid purified by crystallisation from water. It was obtained in colourless needles melting at  $116^{\circ}$ :

0.1035 gave 0.2191  $\text{CO}_2$  and 0.0769  $\text{H}_2\text{O}$ . C = 57.72; H = 8.26.

$\text{C}_8\text{H}_{16}\text{O}_4$  requires C = 57.44; H = 8.51 per cent.

The ethylbutylmalonic acid was decomposed by heating to  $165^{\circ}$  for half an hour. The resulting  $\alpha$ -ethylhexoic acid boiled at  $225^{\circ}$ . The acid was converted into the *amide* by Aschan's method (*loc. cit.*). It crystallised from water in long needles melting at  $101\text{--}102^{\circ}$ :

0.1454 gave ammonia which neutralised 10.30 c.c.  $N/10 \text{ H}_2\text{SO}_4$ . N = 9.7.

$\text{C}_8\text{H}_{17}\text{ON}$  requires N = 9.8 per cent.

The barium salt of the acid has been previously described by Raupenstrauch (*Monatsh.*, 1887, 8, 115), who obtained the acid by the oxidation of the corresponding alcohol. Raupenstrauch states that the barium salt is amorphous. This was confirmed by preparing the barium salt of the synthetic acid which was also found to be amorphous.

$\alpha$ -Ethylhexoic acid is therefore easily distinguished from *n*-octoic acid

by the melting point and crystalline form of its amide, and also by the fact that *n*-octoic acid gives a crystalline barium salt, whereas *n*-ethylhexoic acid does not.

In conclusion, I wish to express my thanks to Dr. Leathes for much kind help and advice during the course of the work.

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CLXXVI.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part X. Effect of the Configuration and Degree of Saturation of the Solvent.*

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IN the last part of this investigation (Trans., 1907, **91**, 504; see also *Ber.*, 1907, **40**, 2564) it was shown by one of us and Mr. McMillan that relatively small quantities (even 2 per cent.) of benzaldoxime and anisaldoxime affect very markedly the rotation of ethyl tartrate in which they are dissolved. Further, the *syn*-form of the oxime has a much greater effect than the *anti*-form, and it was found possible to follow the spontaneous change of the former into the latter by observing the slow alteration in rotation of the admixed active ester.

According to the theory generally accepted at present, the existence of the two forms of an oxime is to be explained by a difference in the spatial arrangement of the atoms in their molecules, and it is interesting that a difference thus represented as a comparatively insignificant detail of configuration is of such enormous importance so far as rotation is concerned. The effect of substituting *syn*-oxime for *anti*-oxime in a mixture with ethyl tartrate, containing, say, 5 per cent. of oxime, is actually greater than would be caused by replacing water by chloroform.

It seemed therefore desirable to investigate the question a little more fully by ascertaining whether the configurational difference in another pair of solvents is of equally marked effect, and, since an isomerism to some extent analogous to that postulated in the oximes is met with in maleic and fumaric acids, we have prepared

the ethyl esters of these two acids and examined the rotation of ethyl tartrate dissolved in them. The experimental results were as follows.

*Ethyl Tartrate in Ethyl Maleate.*

The ethyl maleate was prepared from the silver salt and pure ethyl iodide. It boiled at 105–106° under 14 mm. pressure. For its density, the following data were obtained:

Temperature...	10°	25.2°	32.5°	44.2°
Density...	1.07898	1.06364	1.05697	1.0445

The ethyl tartrate used had  $\alpha_D^{25.1} + 9.602^\circ$ .

Solution I.  $p = 20.6774$ .\*

$t^\circ$ .	$\alpha_D^{25}$ (100 mm.).	Density.	$[\alpha]_D^{25}$ .
12.0°	+2.912°	1.1024	+12.77°
21.4	3.006	1.0930	13.30
31.1	3.132	1.0833	13.98
41.4	3.220	1.0728	14.52
50.8	3.298	1.0623	15.01

*Densities determined.*

Temperature.....	20.3°	25.95°	33.05°	44.4°
Density .....	1.0943	1.0885	1.0814	1.0698

\*  $p$  = grams of ethyl tartrate per 100 grams of solution.

Solution II.  $p = 79.9368$ .

$t^\circ$ .	$\alpha_D^{25}$ (100 mm.).	Density.	$[\alpha]_D^{25}$ .
13.3°	+7.630°	1.1825	+8.07°
25.2	8.694	1.1702	9.29
33.7	9.068	1.1565	10.46
46.9	10.372	1.1433	11.30
53.3	10.746	1.1417	11.78

*Densities determined.*

Temperature.....	18.15°	22.25°	30.05°	34.25°
Density .....	1.1774	1.1731	1.1652	1.1611

*Ethyl Tartrate in Ethyl Fumarate.*

The ethyl fumarate was prepared from fumaric acid, ethyl alcohol, and concentrated sulphuric acid as described by Purdie (Trans., 1881, 39, 346.) It boiled at 98–99° under a pressure of 14 mm. Density determinations gave the following numbers:

Temperature .....	20.6°	30.23°	33.25°
Density .....	1.05189	1.04210	1.03897

Solution I.  $p=20.67835$ .

$t$ , °C.	$\alpha_D^{20}$ (100 mm.),	Density.	$[\alpha]_D^{20}$ .
11.56	+2.874 <sup>2</sup>	1.0895	+12.76 <sup>2</sup>
29.1	3.022	1.0801	13.53
31.5	3.150	1.0684	14.26
34.8	3.230	1.0606	14.73
51.2	3.354	1.0470	15.49

*Densities determined.*

Temperature.....	15.95°	24.1°	32.3°	42.05°
Density.....	1.0844	1.0760	1.0674	1.0573

Solution II.  $p=79.982$ .

$t$ , °C.	$\alpha_D^{20}$ (100 mm.),	Density.	$[\alpha]_D^{20}$ .
14.6 <sup>2</sup>	+7.826 <sup>2</sup>	1.1769	+8.31 <sup>2</sup>
23.7	8.750	1.1669	9.33
29.8	9.236	1.1605	9.95
49.9	10.028	1.1491	10.91
45.3	10.436	1.1435	11.41

*Densities determined.*

Temperature.....	19.05°	31.3°	37.0°	48.8°
Density.....	1.17178	1.15884	1.1530	1.1409

The behaviour of the two solvents may be compared by means of the following table, giving values for specific and molecular rotation at 20° obtained from the foregoing data:

*Rotation of Ethyl Tartrate.*

	In ethyl fumarate.			In ethyl maleate.		
	$p=0$ .	$p=20.7$ .	$p=79.9$ .	$p=0$ .	$p=20.7$ .	$p=79.9$ .
$[\alpha]_D^{20}$ .....	+15.60 <sup>2</sup>	+13.43 <sup>2</sup>	+8.96 <sup>2</sup>	+15.4°	+13.27°	+8.73°
$[M]_D^{20}$ .....	32.14	27.67	18.50	31.73	27.34	17.95

The numbers reveal the fact that the difference in configuration between maleic and fumaric ester is of very little importance as regards the rotation of the ethyl tartrate dissolved in them. At both concentrations examined, the rotation of the fumaric ester solution is slightly greater than that of the maleic ester solution, but only by an amount which is not much in excess of the experimental error, and which is almost entirely negligible when compared with the corresponding difference in the case of the oximes.

In other directions also, no decided contrast in the behaviour of these esters is discernible. Only a slight difference is noticeable in the temperature coefficients for the  $p=20.7$  solutions, the

specific rotation of the solution in ethyl fumarate increasing on heating somewhat more rapidly than the other.

Although therefore a comparison of these two esters in regard to their solvent action reveals no striking divergence, the behaviour of both substances is of considerable interest when compared with the influence of other solvents. As dilution increases, the rotation of the dissolved ethyl tartrate rises fairly rapidly, but apparently not quite linearly, in both esters, as is shown in the diagram, so that at infinite dilution the rotations would be  $+15.6^\circ$  in ethyl fumarate and  $+15.4^\circ$  in ethyl maleate. The rotation of an ethyl tartrate molecule therefore, surrounded by a very large excess of molecules of maleic or fumaric ester, is practically doubled, and is thus very materially modified. In fact, of the solvents hitherto examined, these two esters are only inferior to water (TRANS, 1901, 79, 180; 1904, 85, 1129) in increasing the rotation of ethyl tartrate.

Having thus determined the influence of these two unsaturated esters, it seemed of interest to include in the investigation the corresponding saturated compound. The result was as follows.

#### *Ethyl Tartrate in Ethyl Succinate.*

The succinic ester was prepared from the acid and ethyl alcohol by saturation with hydrogen chloride. It boiled at  $104-105^\circ$  under 15 mm. pressure.

#### Solution I. $p = 20.6721$ .

$t^\circ$ .	$\alpha_D^{20}$ (100 mm.).	Density.	$[\alpha]_D^{20}$ .
11.6°	+1.874°	1.0800	+8.39°
23.1	2.136	1.0681	9.67
31.6	2.288	1.0595	10.45
44.4	2.502	1.0460	11.57
49.9	2.600	1.0408	12.08

#### *Densities determined.*

Temperature.....	19.35°	25.55°	33.95°	43.3°
Density.....	1.07203	1.06552	1.0567	1.0471

#### Solution II. $p = 79.9261$ .

$t^\circ$ .	$\alpha_D^{20}$ (100 mm.).	Density.	$[\alpha]_D^{20}$ .
13.2°	+6.524°	1.1757	+5.94°
20.8	7.348	1.1677	7.87
34.2	8.580	1.1538	9.30
42.0	9.204	1.1459	10.05
49.0	9.732	1.1385	10.69

#### *Densities determined.*

Temperature.....	20.1°	32.0°	36.75°	42.9°
Density.....	1.1684	1.1562	1.1515	1.1450

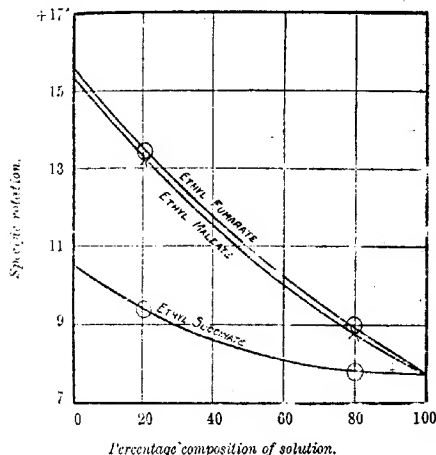


From these data, we obtain for the rotations at 20° the following numbers:

	$p=0$ .	$p=20.87$ .	$p=79.93$ .
$[\alpha]_D^{20}$ .....	+10.5°	+9.35°	+7.80°
$[M]_D^{20}$ .....	21.63	19.26	16.70

The curve for the rotation of ethyl tartrate in ethyl succinate is shown in the diagram. The saturated ester also raises,

*Ethyl tartrate in fumaric, maleic, and succinic ester.*



some extent, the rotation of the tartrate, but its effect in this respect is very considerably less than that of the unsaturated compounds. At infinite dilution, the respective rotations are:

Solvent.	$[\alpha]_D^{20}$ .	$[M]_D^{20}$ .
Ethyl fumarate.....	+15.6°	+32.14°
Ethyl maleate .....	15.4	31.73
Ethyl succinate.....	10.5	21.63

In former papers, it has been suggested that the values for specific rotation and solution-volume of an active substance in different media may be related to each other; in the case of ethyl tartrate, rotation seems to vary inversely with volume. Values for solution-volume, however, do not possess much significance, except for very dilute solutions, and in the present case, owing to the expense of the fumaric and maleic esters, we have not examined any such. Nevertheless, we have calculated the molecular

solution-volumes of the ethyl tartrate in the solutions of  $p=20.67$ . Unfortunately, by an oversight, the density of the succinic ester with which the observations recorded above were made was not determined. A fresh specimen gave these numbers:

*Ethyl Succinate.*

Temperature .....	19°	24.8°	28.04°	31.75°
Density .....	1.0416	1.03543	1.03228	1.02841

A solution of ethyl tartrate in this ester, of  $p=20.6699$ , gave  $d_{20}^{20} = 1.07102$ .

*Molecular Solution-volume of Ethyl Tartrate.*

Solvent.	$p$ .	$d$ .	$\delta$ .	M.S.V. <sup>20°</sup> .	$[\alpha]_D^{20}$ .
Ethyl fumarate.....	20.67835	1.08021	1.0525	171.44 c.c.	+13.43°
Ethyl maleate .....	20.6774	1.08481	1.06892	170.74 "	13.27
Ethyl succinate.....	20.6699	1.07102	1.04050	170.72 "	9.35

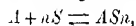
The molecular volume of ethyl tartrate is 170.91, so that there appears to be some slight expansion in the fumaric ester solution, and a trifling contraction in the solutions in maleic and succinic ester, but the changes are only very small and scarcely sufficient from which to draw any definite conclusions. So far as they go, the results are not in accordance with the suggestion mentioned above, since with practically the same solution-volume in ethyl maleate and ethyl succinate the rotations are distinctly different, whilst with slightly different solution-volume in ethyl fumarate and ethyl maleate the rotations are very nearly equal.

The idea that solution-volume and rotation are causally related does not necessarily involve any assumption as to the mechanism of solution, but is certainly simplest if solute and solvent be regarded as entirely independent, a view which has been tacitly adopted hitherto in the present investigation. At its inception, the modern theory of solution included this assumption, and for fairly satisfactory reasons. Gradually, however, opinion has altered to such an extent that at the last meeting of the British Association, "Prof. Abegg reminded Prof. Armstrong that combination between solute and solvent is admitted by everyone."\* It is perhaps to be regretted that such grounds for this admission as can be advanced are not so convincing as the statement itself is concise, and we incline to the belief that the question may at present be regarded as absolutely an open one, although Abegg disposes of the matter in the following simple manner (*Zeitsch. anorg. Chem.*, 1904, 39, 353): "Ferner gehört in diese Gruppe das grosse

\* Report in *Nature*, 1907, 76, 460.

Gebiet der Lösungen die nach unsern Ausführungen zum grössten Teil ebenfalls als lose Verbindungen von gelöstem Stoff und Lösungsmittel aufzufassen sind. . . . Eine chemische Lösung in unserm Sinne liegt in allen Fällen vor, wo beim Vermischen der Komponenten Wärmetönungen, Volumänderungen, optische Änderungen eintreten, kurz wo die Mischung nicht absolut additiv die Eigenschaften ihrer Bestandteile repräsentiert."

Now the suggestion that rotation changes in solution are due to the formation of loose and easily dissociated molecular compounds is a perfectly legitimate one, but it must be consistently worked out. It by no means follows, for instance, that because the volume of a mixture was exactly the sum of the volumes of its constituents therefore no complex-formation had occurred. Abegg's next remark is sufficient to destroy any faith which might be inspired by the confidence of the statement just quoted. "Als physikalische Mischungen ohne chemische Bindung sind auch die idealen verdünnten Lösungen aufzufassen, die ja durch das Fehlen der obigen Erscheinungen definiert sind. Bei ihnen ist die chemische Kraft zwischen Lösungsmittel und gelöstem Stoff . . . so gering geworden, dass der Zerfall der bei höhern Konzentrationen vorhandenen Lösungsverbindungen praktisch vollkommen ist" (*loc. cit.*, 351). This statement suffers from two most serious defects. Firstly, it involves the very difficult question as to the point at which concentrated solutions end and dilute solutions begin. According to Abegg, they differ in character. Therefore it would be necessary to ascribe change of rotation in concentrated solution to combination, and in dilute solution to some other cause not specified. Secondly, the statement is unfortunately a flat contradiction of the law of mass action. If an active substance,  $A$ , combine with solvent,  $S$ , according to the equation:



then obviously the greater the proportion of solvent present the greater will be the percentage number of molecules which combine with solvent molecules, and the greater should be the alteration in the *specific rotation* of the active compound. If  $C$ ,  $C_1$ , and  $C_2$  be the concentrations of  $A$ ,  $B$ , and  $AB_n$  respectively, then

$$KC_2 = CC_1^n,$$

and, since most of the quantities occurring in this equation cannot meanwhile be determined for solutions such as those dealt with here, it is impossible to compare the rate of formation of complex molecules with the rate of change of rotation. When it is borne in mind that this is the simplest statement of the matter, and that perhaps other equilibria must be taken into account before a satisfactory agreement between theory and experiment could be

suggested for, it seems clear that the possibility of attacking the problem from this side is somewhat remote.

Nevertheless, we think that the data recorded in this paper may be discussed in regard to combination between solute and solvent, since it is possible to institute what is probably a legitimate comparison between the solutions which we have examined, on the one hand, and actual chemical compounds on the other.

Thus it is an interesting fact that an unsaturated radicle in an active molecule has a much greater effect on the rotation of the compound than the corresponding saturated radicle.

Thus Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 569) found these data:

Diamyl fumarate .....	$[M]_D^{20}$	+15.17
Diamyl succinate .....	"	9.70

Rupe (*Lanalen*, 1903, **327**, 157) gives values proving a similar behaviour for various menthyl esters. For instance:

Menthyl crotonate .....	$[M]_D^{20}$	-293.1°
Menthyl butyrate .....	"	164.7
Menthyl benzoate .....	$[\alpha]_D^{20}$	-83.53°
Menthyl hexahydrobenzoate .....	"	59.11

Haller and Muller (*Compt. rend.*, 1899, **128**, 1370) found:

Benzylidenecamphor .....	$[\alpha]_D$	+421.25°
Benzylcamphor .....	"	181.82

In each case, the asymmetry of the molecule is increased by the conversion of a single into a double bond, and, although it would be rash to assert that this behaviour will occur in all cases, it seems, so far as we know at present, to be general.\*

If, then, combination occur between ethyl tartrate and ethyl fumarate, on the one hand, and between ethyl tartrate and ethyl succinate, on the other, it might be expected that the former solution should have the higher rotation, and this is indeed the case. At infinite dilution, we find:

Ethyl tartrate in ethyl fumarate .....	$[M]_D^{20}$	+32.14°
Ethyl tartrate in ethyl succinate .....	"	21.63

The difference of 10.51° is thus considerably greater than that found by Walden (5.47°) on comparing the rotations of actual compounds.† The rotation difference is thus quite significant.

Nevertheless, some reservation is necessary, since Rupe's experiments show that the position of the double bond in the molecule is an important factor in determining the rotation. At a distance from the point of attachment of the radicle to the rest of the molecule it has very little effect.

The amyl alcohol used by Walden was not pure and therefore the difference, 5.47°, is too small.

enough to justify the view that it may be due to combination of active substance and solvent.

There is, however, another side to this argument, for Wadley has found that the *l*-amyl esters of fumaric and maleic acids differ considerably:

<i>Di-l</i> -amyl fumarate .....	[M] <sub>D</sub>	+15.17°
<i>Di-l</i> -amyl maleate.....	"	11.82

Consequently, it might be expected that if ethyl fumarate and ethyl maleate combine with ethyl tartrate in solution, there should be a much more distinct difference in rotation than actually exists.

It is thus evident that the argument on one side of this question is opposed by one equally or almost equally strong on the other, but the importance of the problem will, we hope, justify a discussion from which, for our own part, we do not venture, meanwhile, to draw any definite conclusion.

THE UNIVERSITY,  
GLASGOW.

## CLXXVII.—Two Volumetric Methods for the Determination of Chromium.

By ARNOLD WILLIAM GREGORY, B.Sc. (LOND.), and JAMES McCALLUM.

### I.

When ammonium persulphate is added to a solution of a chromium salt in the presence of silver nitrate and nitric acid, the chromium is oxidised to chromic acid.

Upon this reaction, H. E. Walters (*J. Amer. Chem. Soc.*, 1905, **27**, 1550) bases a method for the determination of chromium in steel. In this case, the manganese present is converted into permanganic acid, and the chromium into chromic acid. These two are estimated together by means of ferrous sulphate solution, and the permanganic acid alone by means of sodium arsenite.

This method, although capable of giving good results, has the objection that the chromium is determined by difference, and an appreciable error may thus be introduced where only small quantities of chromium are present.

Kleine (*Stahl und Eisen*, 1905, **25**, 1305; 1906, **26**, 396) removes manganese by first treating a solution of steel in nitric acid with persulphate alone. The manganese is thus converted into manganese dioxide, and may be filtered off. He then removes iron

by extracting the solution with ether, and estimates chromium in the aqueous solution by the persulphate-silver nitrate method.

This process is long, and the removal of the iron appears to us to be a superfluous operation.

The following process has been found to give trustworthy results, and it requires a minimum of time for its performance.

If manganese is absent, the solution is acidified with nitric acid and 20 c.c. of a 1 per cent. solution of silver nitrate added. To this mixture, about 10 grams of ammonium persulphate are added, and the solution boiled for five minutes. The chromium is thus converted into chromic acid, and the excess of the persulphate is decomposed. In order to make quite certain that no persulphate exists in this solution, a few c.c. of a dilute solution of manganese sulphate are now added. If persulphate is present, permanganic acid will be formed, and this may be decomposed by adding a dilute solution of hydrogen peroxide, drop by drop, until the permanganate colour just disappears. (A large excess of hydrogen peroxide must not be used, or reduction of the chromate may occur.)

The solution is once more brought to the boiling point, to expel oxygen, and then cooled and diluted. An excess of standard ferrous sulphate solution is now added, and the excess titrated back with standard dichromate solution. From the data so obtained, the amount of chromium may be calculated.

In the determination of chromium in iron and steel containing manganese, the process is as follows. Two grams of the iron or steel are dissolved in as little nitric acid as possible, and silver nitrate and persulphate added in the usual way. The solution is boiled for a few minutes, and a quantity of ammonium chloride solution is added, such that nearly all the silver is precipitated as chloride. On boiling, the permanganic acid is partly converted into manganese chloride and partly decomposed with the formation of hydrated oxide of manganese. The solution is now diluted to a definite volume, and filtered through an asbestos filter. A quantity of the filtrate, equal to one-half the original volume of the solution, is taken and treated in the same manner as described in the preceding process. The fact that silver nitrate is present in excess during the whole of the process, precludes the possibility of free chlorine being present in the solution.

In making up the solution to a definite volume, no account is taken of the volume of the precipitate, but, as the percentage of chromium present in iron and steel is comparatively low, no appreciable error is introduced on this account.

By working with sufficiently dilute standard solutions, the merest traces of chromium may be accurately determined by this method.

Instead of using a solution of ammonium chloride, a dilute solution of hydrogen peroxide may be employed to reduce the permanganic acid.

We attempted to estimate manganese and chromium simultaneously by converting into permanganic and chromic acids, respectively, and then titrating the former with hydrogen peroxide until the pink colour disappeared, whereupon the chromic acid remaining was titrated with ferrous sulphate solution.

The results obtained were, however, untrustworthy, since oxidation of the chromic acid to perchromic acid began before all the permanganic acid was reduced by the hydrogen peroxide.

#### EXPERIMENTAL.

A solution was made of two grams of chromium-free steel in nitric acid, and to this, 10 c.c. of a solution of chromium sulphate were added. (1 c.c. = 0.003 gram of chromium.)

After oxidation, 28 c.c. of ferrous sulphate were added. On titrating back with potassium dichromate solution (1 c.c. = 0.003 gram of chromium), 1.2 c.c. were required. Ten c.c. of the potassium dichromate solution were equivalent to 24.8 c.c. ferrous sulphate solution:

Found, Cr = 0.0302 gram.

Used, Cr = 0.0300 gram.

Varying amounts of chromium were taken, and equally good results were obtained.

## II.

### *Oxidation by Means of Sodium Bismuthate.*

When sodium bismuthate is added to a solution of a steel containing chromium, the chromium is oxidised to chromate. This reaction takes place instantly if the solution is boiled. At the same time, the manganese is converted into permanganic acid (Abbott and Brearley, *Chem. News*, 1901, **84**, 247, 269). On boiling, the manganese is precipitated as manganese dioxide.

We have obtained excellent results by proceeding in the following manner. Two grams of the iron or steel are dissolved in nitric acid, and about 3 grams of sodium bismuthate added in small quantities. The solution is then boiled until all the manganese is precipitated as dioxide. A small quantity of very dilute hydrochloric acid is now added, whereupon the manganese dioxide is dissolved. Excess of silver nitrate is then added, and the solution boiled, when silver chloride is precipitated. The solution is filtered through an asbestos filter, and titrated in the usual way.

## EXPERIMENTAL.

solution was made of 2 grams of chromium-free steel in nitric acid, and to this, 20 c.c. of a solution of chromium sulphate were added. (1 c.c.=0.003 gram of chromium.)

After oxidation, 51 c.c. of ferrous sulphate solution were added. The excess of ferrous sulphate required 0.5 c.c. of potassium chromate solution. (1 c.c.=0.003 gram of chromium):

Found, Cr=0.0602 gram.

Calcd. Cr=0.0600 gram.

Equally good results were obtained with smaller quantities of chromium.

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CLXXVIII.—*The Atomic Weight of Tellurium.*

By HERBERT BRERETON BAKER and ALEXANDER HUTCHEON  
BENNETT.

THE exception to Mendeléeff's periodic classification presented by this element has led to an enormous amount of work being done on the subject during recent years. Since the atomic weight is about 7 above that of iodine, tellurium appears to fall into a position remote from its congeners, sulphur and selenium. Many hypotheses have been offered to explain the reason of this; Brauner, who worked at the problem for six years (*Trans.*, 1889, **55**, 382), believed that tellurium is not a homogeneous substance, but that "it is a mixture of two elements which cannot be separated by ordinary chemical means" (*Watts Dict.*, **4**, 652, *private communication*). Croft (*Proc.*, 1902, **18**, 112) from a consideration of the differences of the atomic weights of the elements in this group from those of their neighbours came to the conclusion that the atomic weight of tellurium should be above that of iodine. Since 1839, no less than seventeen papers have been published on this subject; in fact, this element has had its atomic weight more rigidly scrutinised than thorium during this period.

Our own work began in 1894, and has been carried on continuously for the last thirteen years. It originated in the discovery made of us (Baker, *Phil. Trans.*, 1888, **179**, 571) that tellurium is one of the few elements which will burn in dried oxygen. It was thought that, since the combustion of carbon disulphide con-



taining elements which do not so burn, is unaffected by the presence of moisture, tellurium might prove to be a compound. The element has been obtained from several sources, namely, from Bohemian tellurium, from West Australian gold ores, from South American copper ores, and lastly, a specimen prepared by Prof. Divers from Japanese sulphur deposits was used. The purification of the element was, in addition to special treatment described later, conducted as follows. The substance was dissolved in *aqua regia*, evaporated several times with hydrochloric acid, diluted with water containing a little sulphuric acid, filtered, and saturated with sulphur dioxide. In this way, most of the gold, silver, bismuth, lead, thallium, and selenium was removed. After washing and drying, the finely-divided element was fused with sodium and potassium cyanides in a current of coal gas. This operation was most conveniently carried on in a porcelain basin covered by another basin, a clay pipe carrying coal gas being inserted in the space formed by the two lips of the basins. The mass on cooling was introduced into a large flask provided with a reverse filter, a tube leading in coal gas, and a tap funnel. Previously boiled water was added, and the red liquid drawn through the filter into a large filtering bottle. By drawing a current of air through the solution the tellurium was precipitated in long, needle-shaped crystals. After very thorough washing, the tellurium was converted into telluric acid by the action of nitric and chromic acids. After many recrystallisations, the acid was dried and heated, the dioxide produced was dissolved in hydrochloric acid, and the solution reduced either by sulphurous acid or by hydrazine hydrate. The element was finally distilled in the purest hydrogen obtainable, prepared by the electrolysis of very pure barium hydroxide solution.

#### *Attempts to Separate Tellurium into Two Elements.*

##### I.

On the hypothesis that another element is present of higher atomic weight in the same group, a separation might be expected by the fractional crystallisation of the acid. Since sulphuric acid, selenic acid, and telluric acid form a series of increasing insolubility in water, one might expect that the acid formed by the unknown element would be obtained in the first fractions of the recrystallised telluric acid.

The telluric acid was obtained by two distinct methods. In the first method (Berzelius), the element was oxidised by nitric acid to which a small quantity of hydrochloric acid was added. The oxide was fused with sodium nitrate, giving a mixture of the normal and

meta-tellurates. The latter is not only insoluble in water and alkalis, but is not decomposed by long boiling with *aqua regia*. The solution of the tellurate was precipitated by barium hydroxide, which had been recrystallised eight times, and the barium tellurate decomposed by boiling with defect of dilute sulphuric acid. The solution of telluric acid was fractionally crystallised.

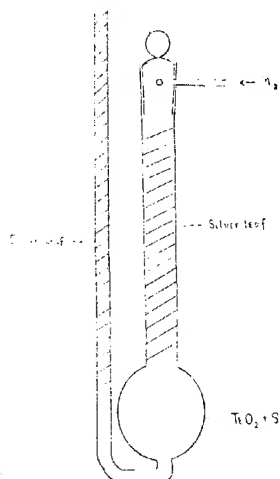
The second preparation of the acid, which, if the tellurium were a mixture, would probably give different results, was carried out by the process recommended by Staudemaier (*Zeitsch. anorg. Chem.*, 1895, 10, 189). The element was dissolved in nitric acid, and to the strongly acid solution the equivalent quantity of chromium trioxide was added. After boiling for an hour, the telluric acid crystallised out on standing. The crystals were drained on an asbestos filter, and by washing with alcohol they were obtained nearly free from chromium nitrate. By recrystallising four times, the acid was obtained in beautiful crystals, free, as far as could be detected by chemical testing, from all impurities. The acid contains two molecules of water of crystallisation.

A large number of determinations of the equivalent were made by heating a weighed quantity of the acid, and weighing the residual dioxide. In spite of all precautions, constant results could not be obtained, the variation in twenty-six determinations being from 126.8 to 128.2. There is no doubt that in this, as in several other cases of salts containing water of crystallisation, the water is not a truly constant amount. Two further methods were attempted in order to surmount this difficulty.

The first was to obtain the ratio of  $\text{TeO}_2 : \text{O}$  in the acid. The weighed acid was contained in a tube of hard glass connected by a ground joint with a small condenser to a Töpler pump. On heating the acid in the evacuated tube, the oxygen was collected in the pump, the water being condensed on the way, and the gas afterwards measured in a carefully calibrated gas pipette. The results were unsatisfactory; however carefully the heating was begun, a little spurring of the acid in the vacuum could not be prevented, and the method was abandoned. The second attempt to determine the same ratio was to heat the acid in a hard glass tube in a current of nitrogen, the oxygen being absorbed in a second tube containing red-hot copper. The results were, however, not constant, and another method was employed, which, as far as we can find, has only been used once before, in a single determination by Berzelius of the equivalent of arsenic. The method is a very elegant one, which is applicable to many elements which lie on the border line between the metals and the non-metals. It consists in weighing a quantity of the oxide in a special tube (Fig. 1), adding highly purified

sulphur, and packing the two ends of the tube with pure silver wool. The tube is weighed again. It is then filled with dried  $\text{nitrogen}$ , and the mixture heated with the smallest flame of an Argand burner. The reaction between the sulphur and the oxide begins at  $130^\circ$ , and proceeds slowly, being complete in about an hour. The silver most effectively stops any loss of sulphur vapour, and the loss in weight of the tube is due to sulphur dioxide only, from which the percentage of oxygen in the oxide of tellurium is readily calculated. The results of the experiments are given below, the weights being calculated to vacuum standard, and assuming  $\text{O} = 16$ ,  $\text{S} = 32.06$ .

FIG. 1.



*Fractional Crystallisation of Telluric Acid Prepared from Barium Tellurate (26 grams of acid used).*

Fraction.	Weight of tellurium dioxide taken.	Loss in weight (sulphur dioxide).	Percentage of oxygen in $\text{TeO}_2$ .
I.	1.5156g	0.00838	20.055
II.	1.02875	0.11074	20.031
III.	1.02150	0.30993	20.046
IV.	0.90835	0.36472	20.053
V.	1.00702	0.40451	20.062
VI.	1.01515	0.40733	20.044

*Second Crystallisation of Telluric Acid Prepared by Oxidising the Element with Nitric and Chromic Acids (167 grams of acid used).*

Fraction.	Weight of tellurium dioxide used.	Loss in weight (sulphur dioxide).	Percentage of oxygen in $\text{TeO}_2$ .
I.	1.56837	0.62938	20.046
II.	1.07852	0.43257	20.035
III.	1.72627	0.69296	20.052
IV.	2.09253	0.82927	20.032
V.	0.83335	0.33465	20.059
VI.	1.15372	0.46281	20.011
VII.	1.68613	0.67661	20.045
VIII.	0.90835	0.36472	20.053

The results afford no evidence of any separation brought about by the fractional crystallisation of telluric acid.

Mr William Crookes was kind enough to examine spectroscopically the element from the first and last fractions of the crystallisation of telluric acid, series II. The beautiful spectra which he obtained showed the complete identity of the element from the two fractions.

## II.

A second series of experiments on the possible decomposition of tellurium was based on the progressive solubility of the barium salts of the acids, as one descends the series. Barium sulphate is one of the most insoluble salts known, barium selenate less so, whilst barium tellurate is appreciably soluble in water. If therefore tellurium contains an element of higher atomic weight in the same series, the barium salt of its acid ought to be fairly soluble. In order to test this, a quantity of the purest acid used in the last experiments was neutralised with very pure barium hydroxide in concentrated solution, a slight excess of the base was then added, and carbon dioxide passed into the solution to precipitate any uncombined barium hydroxide. The mixture was evaporated to a small bulk on the water-bath and filtered. The precipitate was then washed with 3 litres of distilled water, and the hot liquid filtered off. The solution was evaporated, and the crystallised barium salt thus obtained was converted into the acid by dilute sulphuric acid. This was heated to give the dioxide, and the undissolved barium tellurate was treated in the same way. The atomic weight of the element found in the two specimens of the oxide showed no difference, the numbers being:

From soluble barium tellurate, 127.60  
 „ insoluble „ „ 127.61.

## III.

*Fractional Distillation.*

Experiments were made first on the element, which was fractionally distilled (1) in a vacuum, (2) in the very pure hydrogen obtained by the electrolysis of barium hydroxide solution. The different fractions gave the same atomic weights. The spectra of these fractions were photographed, and showed no difference, the large spectroscope bequeathed to Oxford University by the late Duke of Marlborough being used for this purpose. Since, however, many known tellurides are volatile without decomposition, it was thought that compounds with negative elements or groups might be tried with advantage. The first substance chosen was ethyl telluride, a considerable quantity of this substance being prepared by Wöhler's method. These experiments had to be abandoned, however, owing to the unpleasant physiological effects of the vapour, and the more than repulsive odour which workers with it contract. As our ordinary work during the daytime brought us into contact with many other persons, it was found necessary to choose some less offensive compound. It may be mentioned that clothes worn during the preparation of the substance were left in the open air for a month, and, in spite of their exposure to rain and wind, it was necessary to burn them at the end of this period.

The next substance submitted to fractional distillation was the tetrachloride. The purified element was treated by purified chlorine obtained from pyrolusite and hydrochloric acid. The operation was carried on in a glass tube, to the end of which was sealed a series of seven bulbs in which the fractions were collected. Since chlorine obtained by the method used contains traces of oxygen, it was supposed that, as in the case of antimony chloride, some oxychloride of tellurium might be found. Before the distillation, therefore, a current of hydrogen chloride was passed over the heated chloride, and this was followed by a current of nitrogen. The most rigid precautions were taken to avoid the access of moisture. The tetrachloride thus prepared was almost pure white. The analysis of four fractions was made by dissolving the contents of the bulbs in tartaric acid solution, and adding the silver nitrate from a weighed quantity of silver prepared by Stas's bisulphite method. The precipitation was completed by the addition of  $N/100$  silver nitrate from a weight burette. The atomic weights were:

Fraction	I.	127.58.
"	III.	127.60.
"	V.	127.64.
"	VII.	127.62.

It was thought that in spite of the precautions, oxychloride might well have been formed and not removed, so that a series of fractionations of the tetrabromide was performed, since if very pure bromine is used there is no difficulty in conducting the preparation and distillation in complete absence of oxygen. The bromine used was obtained by the method described by Stas, the purified bromine being distilled from purified zinc oxide and potassium bromide. After the preparation of the bromide, it was found that the substance could not be distilled without dissociation, even if the temperature is kept at the lowest possible point. If the temperature is raised much above the volatilisation point, the vapour breaks up with the manifestation of a multitude of glowing sparks which completely fill the tube. Distillation in a vacuum was found also to produce dissociation, dibromide being visible in each of the bulbs in which the fractions were collected. In order to get rid of this, a current of nitrogen laden with bromine vapour was led through the bulbs, and a current of nitrogen alone was passed for some hours until the issuing gas gave no reaction with potassium iodide and starch. On analysing the fractions, however, the amount of bromine found was much too high, probably owing to a combination or absorption of bromine by the bromide. It was therefore thought to be advisable to choose another substance free from such complications.

*Fractional Distillation of the Dioxide.*—Considerable difficulty was experienced in distilling this substance. It volatilises only at a red heat, and at this temperature it was found to attack porcelain and platinum. Success was ultimately attained by distillation in a quartz tube heated by a small electric resistance furnace. The oxide was obtained from recrystallised telluric acid. Even quartz is so much attacked by the heated dioxide that it was not found possible to obtain a determination from the residue. Hence the comparison was made between the distilled dioxide and a sample of the original dioxide used in the experiment. The determinations were made by the sulphur method described above.

First distilled oxide contained 20.050 per cent. of oxygen.

Original   "       "       20.052   "       "

Hence no difference is caused by this treatment.

#### IV.

##### *Conversion into Tellurium Hydride.*

There is a progressive change in stability of the hydrides of this group as the atomic weight increases, the dissociation of hydrogen sulphide beginning about 500°, that

of hydrogen selenide about  $270^{\circ}$ , whilst hydrogen telluride dissociates at the ordinary temperature. If therefore there is an element in the same group associated with tellurium, it would be expected that its hydride would scarcely be formed at any but very low temperatures. Hence tellurium prepared from the hydride should be free from any element in the same group which had a higher atomic weight.

In the earlier stages of the research, a large amount of work was done in order to find a method of obtaining the hydride of tellurium in quantity. Direct synthesis, the decomposition of the tellurides of potassium and magnesium gave very small yields, but the action of water on aluminium telluride gave rather better results, the yield from 20 grams of tellurium being from 0.1 to 0.3 gram. Some 10 grams of the purified element were accumulated by this tedious process in six months, but by the carelessness of a workman passing through the laboratory the whole of it was lost. In three months more, 6 grams of tellurium were obtained; it was converted into telluric acid by chromic acid, and this after recrystallisation was decomposed into the dioxide.

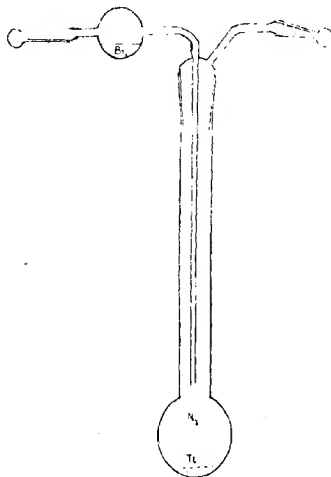
The percentage of the oxygen in this oxide was found in two experiments to be 29.062 and 29.058, thus showing no difference from the original substance. Further experiments on a larger scale were rendered possible by the discovery by Erneyi of an electrolytic method for the production of tellurium hydride. A lump of purified tellurium was made the cathode in the electrolysis of dilute sulphuric acid. The gas passed through a horizontal tube which was heated to about  $150^{\circ}$  in order to decompose the hydride formed. The deposited tellurium was purified from possible contamination of sulphur by fusion with sodium and potassium cyanides, and it was finally distilled in a current of hydrogen prepared by the electrolysis of barium hydroxide. By similarly treating the tellurium which was left in the electrolytic vessel, a comparison could be made directly of the element which had, and that which had not, been converted into the hydride.\*

For these determinations another method was used for the determination of the equivalent. A quantity of the element was powdered in an agate mortar and weighed in the apparatus (Fig. 2), which was made of Jena glass. This was then filled with dried nitrogen, and highly purified bromine (see p. 1855) poured through

\* It is not generally known that tellurium hydride is poisonous. All the time we were working with this gas, we both suffered from severe headaches, although as little as possible of the gas was allowed to escape into the air. On one occasion, one of us inhaled, by accident, a bubble of the gas. It caused a very severe attack of vertigo, which lasted for three days, and was accompanied by a low temperature,  $95.2-95.8^{\circ}$  F.

a drawn-out funnel into the upper bulb. The bromine was added in very small quantities at a time to the powdered tellurium in the lower bulb, and the apparatus allowed to stand, well-stoppered, for twelve hours. It was then heated to  $50^{\circ}$  in a specially constructed air-bath, a current of dried nitrogen being passed through until the issuing gas gave no reaction with potassium iodide, showing that the excess of bromine had been expelled. The nitrogen was displaced by a current of dried air and the apparatus was transferred to the balance case. The method has the advantage of simplicity, and

FIG. 2.



avoids any transference from one vessel to another. The Jena glass proved very resistant to bromine, an apparatus which was used for six determinations showing a loss in weight of less than 0.0001 gram for the whole period. A similar tube was used as a counterpoise, and, since the tetrabromide is somewhat hygroscopic, the tubes were fitted with well-ground stoppers. The apparatus was made of as thin glass as could be procured; when empty, it weighed 12 grams. It was shown that the tetrabromide is unaffected by dried air.

The results of the determinations are given below:



*Tellurium Prepared from the Hydride.*

No.	Weight of tellurium.	Weight of tetrabromide.	Percentage of tellurium.
1.	0.61278	2.14933	28.508
2.	0.56866	1.99354	28.526
3.	0.59884	2.09951	28.523
4.	0.57894	2.03040	28.514
5.	0.54713	1.91899	28.527
6.	0.35859	1.18732	28.517
7.	0.56866	1.99354	28.524
8.	0.47611	1.67025	28.525
9.	0.56922	1.98597	28.511
Mean.....			28.519

The determinations made with the tellurium which remained after the hydride had passed off:

No.	Weight of tellurium.	Weight of tetrabromide.	Percentage of tellurium.
1.	0.41271	1.55205	28.524
2.	0.41671	1.46177	28.508
3.	0.50611	1.77489	28.515
Mean.....			28.516

In the case of the tellurium in determinations 7, 8, and 9, the tellurium hydride was passed through a tube heated by a water-jacket to  $35^{\circ}$ , and only the tellurium hydride which survived this treatment was taken for the source of the tellurium. No difference was apparent in the tellurium obtained in this way.

In order to compare the results of this method with the method of heating the dioxide with sulphur, a quantity of the tellurium from the hydride was converted into the oxide by heating with purified nitric acid. The residue was heated to about  $450^{\circ}$  for several days in order to decompose the last traces of the basic nitrate. Attempts to quicken this operation resulted in failure. When, for instance, the oxide was moistened with ammonia and heated, it acquired a grey tint which was not lost by long-continued heating in air.

*Analysis of Tellurium Dioxide Prepared from Tellurium Hydride.*

No.	Weight of dioxide.	Loss in weight (sulphur dioxide).	Percentage of oxygen in $\text{TeO}_2$ .
1.	1.02217	0.41650	20.064
2.	0.89697	0.32322	20.051
3.	1.32003	0.52492	20.053
4.	1.05207	0.42221	20.047
5.	1.37043	0.54969	20.032
6.	0.95944	0.38511	20.048
Mean.....			20.049

The agreement between the results obtained by the two methods is satisfactory. By the tetrabromide method, the atomic weight (79.96) is 127.601, whilst by the method of reduction by means of sulphur the atomic weight is 127.609.

*Attempt to Separate Tellurium by Fractional Electrolysis.*

These experiments were made at the suggestion of Prof. Abegg and Mr. F. W. Watkin.

About 20 grams of the tellurium which had been converted into the hydride were converted into the tetrabromide, and this was dissolved in the smallest possible quantity of hydrobromic acid. A carbon rod, which had been heated to redness in chlorine and afterwards washed, was placed in a small porous pot and used as the anode. The pot rested on a glass triangle in a large platinum dish, which was the cathode. A current of 0.1 ampere was used, and each fraction was the result of about 12 hours' electrolysis. The deposit in the platinum dish was dissolved by hot concentrated sulphuric acid. The solution was precipitated by sulphurous acid, washed, dried, and distilled in hydrogen.

In the first series of experiments by this method, a high atomic weight (129.02) was obtained from the first fraction. On testing the tetrabromide, however, it was found to contain a trace of platinum. In subsequent determinations, each fraction was fused with potassium cyanide, the solution of potassium telluride filtered off, decomposed by water, and the resulting tellurium then distilled in hydrogen. The results were:

Series II; 25 grams of tellurium tetrabromide used.

Fraction.	Weight of tellurium.	Weight of tetrabromide.	Percentage of tellurium.
1.	0.37382	1.31081	28.519
2.	0.31895	1.11868	28.512
3.	0.48981	1.71554	28.522
4.	0.47156	1.65404	28.510

Series III; 160 grams of tellurium tetrachloride used.

1 (1).	0.10748	1.42867	28.523
1 (2).	0.62013	2.17449	28.518

Through an unfortunate accident, this fractionation could not be continued, but the experiments on the first fraction indicate that this was to be hoped for in the way of separation.

*Attempted Separation by the Decomposition of the Chloride in Water.*

It would be possible that closely-allied elements might be separated to some extent by this method. To find out if this were so, the case of mixed antimony and bismuth chlorides was given to the students working in the laboratory at a course of inorganic chemistry. Somewhat to our astonishment, Mr. Walling, of Magdalen College, succeeded, by cautious addition of water to the mixture, in obtaining a complete separation of antimony from bismuth. The method was then used with tellurium chloride. It was thought that if the chlorides of two elements were present, the precipitation as oxychloride of the one with lower atomic weight would, as in the case of antimony and bismuth, take place first.

About 35 grams of the tetrachloride were dissolved in the minimum quantity of dilute hydrochloric acid and 50 c.c. of water were added. The slight cloudiness which was first formed developed into a precipitate in the course of twelve hours. This was filtered off, reduced by sulphur dioxide, and distilled in hydrogen. The process was repeated and four fractions were obtained, of which the second was by far the largest:

Fraction.	Weight of tellurium.	Weight of tellurium tetrabromide.	Percentage of tellurium.
1.	0.373.2	1.31081	28.519
2.	0.50822	1.78297	28.518
3.	0.12923	0.45354	28.505
(very small)			
4.	0.42926	1.50540	28.515

For the sake of comparison, we add two determinations made with tellurium from the sulphur deposits in Japan. This was kindly lent to us by Prof. E. Divers, who had himself purified it very carefully. It was only thought necessary to redistil it in hydrogen:

*Japanese Tellurium.*

No.	Weight of tellurium.	Weight of tellurium tetrabromide.	Percentage of tellurium.
1.	0.8338	2.81715	28.511
2.	0.95509	3.34193	28.512

The balance used throughout this research was one of Oertling's No. 5, made some twenty-five years ago. The weights were standardised among themselves, and the figures given in the paper are the weights calculated to vacuum standard. The mean of the

twenty-five determinations of the oxygen in tellurium dioxide by the sulphur method gives the percentage as 20.048, the atomic weight of tellurium calculated from this ( $O=16$ ) is 127.609.

The mean of the eighteen determinations of the tellurium in the tetrabromide is 28.518, from which, assuming  $Br=79.96$ , the atomic weight of tellurium is 127.601. Since the latter method is *a priori* the better one, we incline to think that 127.60 is the nearer to the true constant.

*General Conclusions.*—No difference could be distinguished in the atomic weight of tellurium when:

1. Telluric acid, obtained by two distinct methods, was fractionally crystallised;
  2. Barium tellurate was dissolved in water;
  3. Tellurium was fractionally distilled;
  4. Tellurium tetrachloride was fractionally distilled;
  5. Tellurium dioxide was fractionally distilled;
  6. Tellurium was converted into the hydride, and fractionally decomposed;
  7. Tellurium tetrabromide and tetrachloride were submitted to fractional electrolysis;
  8. Tellurium tetrachloride was fractionally precipitated by water.
- The atomic weight of tellurium is 127.60.

Highly purified tellurium does not burn in dried oxygen.

The work was carried on for eight years in the laboratory at Dulwich College, S.E., for one year in a private laboratory, and for the last four years in the new research laboratory at Christ Church.

We wish, in conclusion, to express our thanks to Sir William Crookes for his examination of the spectrum of the element, to Prof. Divers for the loan of Japanese tellurium, and to the Committee of the Research Fund of the Chemical Society for a grant for the purchase of material.

CHRIST CHURCH,  
OXFORD.

CLXXIX.—*Gaseous Nitrogen Trioxide*

By HERBERT BIERETON BAKER, M.A., D.Sc., F.R.S., and MUMFORD BAKER.

NITROGEN trioxide has been shown to exist (Ramsay and Cundall Trans., 1885, 47, 187; Ramsay, Trans., 1890, 57, 590) in the green liquid obtained by the condensation of the gas evolved by the action of nitric acid on arsenic trioxide. It was found that on allowing the liquid to evaporate, almost complete dissociation took place, and the gas consisted almost entirely of nitrogen peroxide and nitric oxide. The discovery by one of us that traces of moisture were necessary for the dissociation of ammonium chloride (Trans., 1894, 65, 616), mercurous chloride, and other substances (Trans., 1900, 77, 645), led us to investigate the question whether, in the dried condition, nitrogen trioxide could be obtained in the gaseous state.

In order to obtain the liquid available for experiment, it was necessary to seal it up in bulbs without contact with atmospheric moisture. In order to do this, a series of ten bulbs was blown on a thin capillary tube the outside diameter of which was about 0.5 mm. The end of this tube was sealed to a tube of about 20 c.c. capacity, and the whole dried by heating while a current of dried air was drawn through. A plug of ignited asbestos was placed in the junction of the capillary and the wide tube, and plugs of redistilled phosphorus pentoxide introduced. The tube was closed and allowed to stand for a week to ensure the drying of the internal surface of the glass. The nitrogen trioxide was prepared by the action of nitric acid (sp. gr. 1.3) on arsenic trioxide. The gas was passed first through a long worm tube cooled by ice in order to condense any nitric acid carried over. It was then dried by a tube of phosphorus pentoxide, and condensed in the tube described above, which was cooled by pounded ice and calcium chloride. When sufficient liquid had been condensed, a current of nitric oxide, dried by phosphorus pentoxide, was bubbled through it for an hour, and the tube sealed. It was left to dry for three weeks. By cooling the bulbs, the liquid distilled over, and by means of a very fine-pointed blow-pipe flame the capillaries between the bulbs were drawn off and the bulbs containing the liquid were washed in distilled water and dried in a desiccator. The sealing off of these bulbs was an operation of extreme delicacy, and many attempts resulted in failure. Sealing by means of a fine, red-hot platinum wire was tried but the method left the ends of the capillaries so thin that they burst when the liquid attained the ordinary temperature.

Many methods were tried before a satisfactory analysis of the liquid could be obtained. Potassium permanganate, potassium iodide, ammonia, and carbamide solution were all tried as reagents for estimating the oxygen or nitrogen, and failed to give constant results. This was also the case with the ordinary nitrometer method with mercury and sulphuric acid, the volume of the nitric oxide evolved being always too small. A possible explanation of the latter fact is that nitric oxide is not the only gas produced. In one experiment, the gas was transferred to another nitrometer and showed considerable contraction when treated with alcohol, and the residue was not all absorbed by ferrous sulphate solution, indicating the presence of nitrogen and nitrous oxide. A direct method was then resorted to. A weighed bulb of the liquid was introduced into a thick-walled Jena glass tube with a piece of glass rod for breaking it. In the other end was placed a weighed roll of copper gauze enclosed in a thin-walled Jena tube open at both ends. The wider tube was then drawn out at each end, filled with dried nitrogen and sealed. The bulb was broken and the part of the tube containing the copper was heated in an improvised furnace for twelve hours. By breaking the capillary end of the wider tube in a thick-walled indiarubber tube, the excess of nitrogen was made to displace water from a wash-bottle into a weighed flask, thus giving a rough estimation of the nitrogen in the trioxide. This estimation must always give results which are too low, since the sealing of the tube, however carefully done, must heat and expand some of the original nitrogen. If it had been possible to use large quantities of the liquid, the error would have been minimised, but attempts to do this led to the explosion of the whole. The oxygen was estimated by the gain in weight of the copper. The results were:

	Weight of liquid.	Increase in weight of copper.	Percentage of nitrogen.	Percentage of oxygen.
1.	0.0856	0.0640	—	63.0
2.	0.1875	0.1189	35.1	63.4
3.	0.1976	0.0667	33.8	62.1
4.	0.0937	0.05980	33.9	63.8
5.	0.1145	0.0722	34.7	63.1

The mean percentage of oxygen is 63.08, that calculated for  $N_2O_3$  is 63.17.

In order to show that the deficiency of nitrogen is really caused as stated above, and not by the presence of dissolved phosphorus pentoxide, a large quantity of the liquid was dissolved in cooled nitric acid, but this produced no colour with ammonium molybdate. The liquid also evaporated in air without leaving any residue. Its composition therefore corresponds to the formula  $N_2O_3$ .

In order to determine the density of the gas evolved by the evaporation of the liquid, weighed bulbs were broken in a Lunge nitrometer over purified and dried mercury. The breaking of the bulb was effected by the pressure of a long glass rod which passed through an indiarubber stopper at the bottom of the nitrometer. The gas has very little effect on dried mercury. The following results were obtained by this method:

	Weight of liquid used.	Time of drying over phosphorus pentoxide.	Temperature.	Pressure.	Density.
1.	0.0645	6 days	15°	770 mm.	43.2
2.	0.0571	27 "	14	747 "	43.6
3.	0.0515	13 "	13	768 "	48.6

On adding concentrated sulphuric acid to the gas, solution took place so rapidly that the rush of the mercury up the tube could not be followed by the eye, and the impact of the metal against the top of the tube threatened its destruction. This observation makes it clear that the gas does not contain a mixture of nitrogen peroxide and nitric oxide, which is shown by experiment to undergo only a comparatively slow absorption by sulphuric acid.

Other determinations of the density of the gas were made in a special form of V. Meyer's apparatus, which has been described by one of us (*Trans.*, 1900, **77**, 647). The weighed bulb of liquid was placed at the bottom of the cylindrical bulb of the apparatus and the movable glass spoon was used to support a piece of heavy glass rod. On turning the spoon, the rod dropped on to the bulb, so liberating the liquid. In order that the rod should hit the bulb, it was found necessary to seal a perforated glass tube inside the apparatus to act as a guide. The apparatus was dried by heating while a current of nitrogen was passed through. The sealed tube which formed the stopper of the apparatus contained phosphorus pentoxide, and the exit tube, which was connected with a gas-measuring apparatus, was filled with the same substance. The drying of the apparatus by the phosphorus pentoxide was continued through varying periods as shown in the table on page 1865.

The density of undissociated  $N_2O_3$  is 38, and hence the gas obtained in these experiments must contain a higher polymeride, probably  $N_4O_6$ , corresponding to the analogous oxides of phosphorus and arsenic. It will be noticed that there is a large variation in the densities obtained in the different experiments, and it should be mentioned that the bulbs used came from not less than eight different preparations, the liquid in which was condensed at different temperatures, and which was allowed different lengths of time to dry in contact with the phosphorus pentoxide. We hope that it

No.	Weight of liquid.	Time of drying of the vapour density apparatus in days.	Temperature.	Pressure in mm.	Density.
1.	0.0649	23	22°	758	38.1
2.	0.0598	4	21	744	38.4
3.	0.0241	14	22	752	41.5
4.	0.0487	6	20	735	42.0
5.	0.0160	6	15	755	42.1
6.	0.0902	20	18	757	42.8
7.	0.0452	6	22	745	42.8
8.	0.0382	14	20	744	40.0
9.	0.1034	8	18	756	40.3
10.	0.0299	28	21	742	57.0
11.	0.1475	22	17	802	59.2
12.	0.0493	7	18	739	59.8
13.	0.0134	33	60	613	62.2

may be possible by drying the liquid at a lower temperature to obtain the higher polymeride in a pure condition.

In order to compare the behaviour of the dried and undried liquid, the same apparatus was used for determining the density of the liquid which had been contaminated by a trace of moisture. This was effected by opening the capillary of the bulb, immersed in a freezing mixture, for a few seconds and then sealing it up. The first difference noted during the density determination was that the boiling liquid rapidly lost its green colour, leaving a yellow liquid which then disappeared, whilst with the dried liquid there was no change in colour as it boiled away. The density given by this moist liquid was 28.2, the temperature being 22°. If it is calculated what density would be given by  $N_2O_3$  breaking up into  $N_2O_4$ ,  $NO_2$ , and  $NO$  at 22°, a density of 27.8 is found, so that in presence of a mere trace of moisture practically complete dissociation of the liquid takes place.

Some determinations of the molecular weight by the lowering of the freezing point of purified and dried benzene were made, to see if at the temperature of 4° and in solution the higher polymeride would be in a more concentrated state. This was not found to be the case. Two bulbs from the same preparation were used in the first case, and one from another preparation in the second.

I. (a) 0.1364 of liquid in 10.2 of benzene gave depression 0.8°. M.W. = 83.

(b) 0.0455 of liquid in 10.3 of benzene gave depression 0.26°. M.W. = 83.2.

II. 0.0627 of liquid in 10.8 of benzene gave depression 0.29°. M.W. = 95.

In these experiments, the benzene was dried over distilled phosphorus pentoxide, and care was taken that the thermometer and the



tube in which the experiment was done were as far as possible dried to a similar extent. The dried benzene was quite unaffected by the dried trioxide. After a very short exposure to moist air, the solution lost its green colour, at the same time giving off nitric oxide with effervescence, leaving a yellow solution of nitrogen peroxide.

We hope in a future communication to describe the physical and chemical properties of nitrogen trioxide. Its specific gravity in the state of liquid is about 1.11. The liquid has a green colour at the ordinary temperature, but, when cooled to  $-2^{\circ}$  or below, the colour changes to a deep indigo-blue. The liquid shows no signs of freezing in a mixture of solid carbon dioxide and ether at  $-81^{\circ}$ , but in liquid air it forms very deep blue crystals. It is very little, if at all, soluble in water. When a bulb is broken under ice-water, the liquid sinks to the bottom of the vessel, giving off nitric oxide and nitrogen peroxide, the latter dissolving in the water. The gas is very soluble indeed in concentrated sulphuric acid.

#### *Addendum.*

In order to ascertain if similar polymerisation takes place with nitric oxide and carbon monoxide, these gases were introduced into tubes containing phosphorus pentoxide, which were connected with manometers. The tubes were then cooled with liquid air, so that the liquefied gases were in contact with the drying agent. The drying at the low temperature was continued for four days. On regaining the ordinary temperature, the gases showed no change in volume, so that in these circumstances no polymerisation takes place.

The work has been done in the new research laboratory at Christ Church.

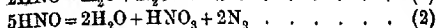
CHRIST CHURCH,  
OXFORD.

### CLXXX.—*The Decomposition of Hyponitrous Acid in Presence of Mineral Acids.*

By PRAFULLA CHANDRA RAY and ATUL CHANDRA GAṄGULI.

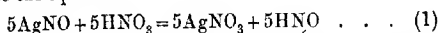
HYPONITROUS acid has been isolated by Hantzsch and Kaufmann, who have also described some of its important properties and its decomposition products (*Annalen*, 1896, 292, 317). In continuation of our work on the decomposition of silver and mercurous hyponitrites we have recently studied the action of mineral acids on these salts at the

ordinary temperature, namely, 25—29°. It will be shown that the hyponitrous acid which is set free decomposes simultaneously according to the two equations:

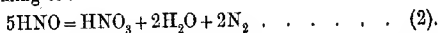


*Silver Hyponitrite and Nitric, Hydrochloric, and Sulphuric Acids.*

*Method of Experiment.*—In order to avoid unnecessary repetition the details of experiments will be given here once for all. The substance was weighed in a tube, and another tube, much narrower in diameter, and containing from 1 to 2 c.c. of dilute nitric acid, was placed in it. The apparatus, after exhaustion by means of a Sprengel pump, was gently tilted so as to bring the salt and the acid into contact with each other. Brisk effervescence at once set in. The gaseous product which was found to be free from nitric oxide was analysed in the following manner. It was repeatedly shaken up with tap water,\* changing the water if necessary, until no more absorption took place. The remaining gas which was unaffected by alkaline pyrogallate was taken to be nitrogen. The residue in the tube did not respond to Nessler's or Fehling's solution and was thus absolutely free from ammonia and hydroxylamine. It was also found to be free from nitrite. The amount of nitrate in it was estimated by making it up to a given volume and treating an aliquot portion by the Crum-Brankland method. An example will make the point clear. Let us assume that the first reaction which set free hyponitrous acid was according to the equation:



and that the second reaction which gave rise *de novo* to nitric acid was that conforming to:



In the experiment in question 1 c.c. of dilute nitric acid was used. As a blank test, 1 c.c. of this acid was made up to 20 c.c., of which 1 c.c. again gave 3.9 c.c. of nitric oxide. The residual product was also made up to the same bulk (20 c.c.) and 1 c.c. of it yielded 4.1 c.c. of nitric oxide. The difference was 0.2 c.c. of nitric oxide. Now  $20 \times 0.2$  c.c. or 4 c.c. was the total amount of nitric oxide and half of it, namely, 2 c.c., as nitrogen, represented the nitric acid generated according to the equation (2). The free nitrogen which was measured according to the process described above was actually found to be

That is, with water saturated with respect to nitrogen at the ordinary temperature and pressure. By blank experiments we have satisfied ourselves that it is a fully trustworthy method of estimating the proportion of nitrous oxide and nitrogen in a mixture of the two gases.

8.2 c.c. at the same temperature and pressure; hence the ratio of nitrogen in nitric acid to nitrogen in the free condition was as 1:1. When sulphuric or hydrochloric acid was used no blank experiment was, of course, necessary.\*

*Decomposition of Silver Hyponitrite.*

(a) With nitric acid (1 c.c. = 0.179 gram of  $\text{HNO}_3$ ).

- Expt. I. 0.1764 gave 11.5 c.c. N as such, 2.88 c.c. N as  $\text{HNO}_3$ , and 2.0 c.c.  $\text{N}_2\text{O}$ ;  $t = 25^\circ$ ;  $p = 760$  mm.  
 Expt. II. 0.1916 gave 6.1 c.c. N as such, 1.5 c.c. N as  $\text{HNO}_3$ , and 1.9 c.c.  $\text{N}_2\text{O}$ ;  $t = 25^\circ$ ;  $p = 760$  mm.  
 Expt. III. 0.1218 gave 8.2 c.c. N as such, 2.05 c.c. N as  $\text{HNO}_3$ , and 1.3 c.c.  $\text{N}_2\text{O}$ ;  $t = 27^\circ$ ;  $p = 760$  mm.

(b) With hydrochloric acid (1 c.c. = 0.153 gram of  $\text{HCl}$ ).

- Expt. I. 0.2144 gave 13.4 c.c. N as such, 3.4 c.c. N as  $\text{HNO}_3$ , and 3.1 c.c.  $\text{N}_2\text{O}$ ;  $t = 26^\circ$ ;  $p = 760$  mm.

(c) With sulphuric acid (1 c.c. = 0.366 gram of  $\text{H}_2\text{SO}_4$ ).

- Expt. I. 0.17 gave 5.2 c.c. N as such, 1.3 c.c. N as  $\text{HNO}_3$ , and 8.7 c.c.  $\text{N}_2\text{O}$ ;  $t = 27^\circ$ ;  $p = 760$  mm.  
 Expt. II. 0.115 gave 4.8 c.c. N as such, 1.2 c.c. N as  $\text{HNO}_3$ , and 4.9 c.c.  $\text{N}_2\text{O}$ ;  $t = 31^\circ$ ;  $p = 760$  mm.

The results of these experiments are tabulated below; the figures denote percentages:

(a) With nitric acid:

No. of expt.	N as such.	N as $\text{HNO}_3$ .	N as $\text{N}_2\text{O}$ .	Total N found.	Total N (theory).
I.	7.25	1.81	1.26	10.32	10.14
II.	6.72	1.65	2.09	10.46	"
III.	7.45	1.86	1.18	10.49	"

(b) With hydrochloric acid:

I.	6.95	1.74	1.61	10.30	10.14
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(c) With sulphuric acid:

I.	3.39	0.85	5.70	9.94	10.14
II.	4.52	1.13	4.58	10.23	"

\* It may be noted here that as the Crum-Frankland method is not satisfactory in presence of a chloride the nitric acid in this case was tested by Pelouze's method.

† The gases were always measured in the moist state.

*Mercurous Hyponitrite and Nitric, Sulphuric, and Hydrochloric Acids*

The method of experiment was the same as described before, and no further prefatory remarks are called for. The only point to bear in mind is that a solution of mercurous hyponitrite in dilute nitric acid undergoes slow dissociation; thus:  $\text{Hg}_2(\text{NO})_2 = \text{Hg} + \text{Hg}(\text{NO})_2$ . As the acid was very dilute and as the reaction was completed in a few minutes there was no appreciable disturbance due to secondary reaction, namely, interaction between metallic mercury and excess of nitric acid.

*Decomposition of Mercurous Hyponitrite.**(a) With nitric acid.*

Expt. I.—0.197 gave 6.3 c.c. N as such, 1.58 c.c. N as  $\text{HNO}_3$ , and 1.0 c.c.  $\text{N}_2\text{O}$ ;  $t = 28^\circ$ ;  $p = 760$  mm.

*(b) With hydrochloric acid.*

Expt. I.—0.115 gave 4.0 c.c. N as such, 1.0 c.c. N as  $\text{HNO}_3$ , and 1.6 c.c.  $\text{N}_2\text{O}$ ;  $t = 31^\circ$ ;  $p = 760$  mm.

Expt. II.—0.25 gave 9.3 c.c. N as such, 2.33 c.c. N as  $\text{HNO}_3$ , and 2.4 c.c.  $\text{N}_2\text{O}$ ;  $t = 30^\circ$ ;  $p = 760$  mm.

*(c) With sulphuric acid.*

Expt. I.—0.1955 gave 2.8 c.c. N as such, 0.7 c.c. N as  $\text{HNO}_3$ , and 5.2 c.c.  $\text{N}_2\text{O}$ ;  $t = 25^\circ$ ;  $p = 760$  mm.

The results are presented below in percentages in a tabulated form:

*(a) With nitric acid:*

No. of expt.	N as such.	N as $\text{HNO}_3$ .	N as $\text{N}_2\text{O}$ .	Total N found.	Total N (theory).
I.	3.55	0.89	0.56	5.0	6.09

*(b) With hydrochloric acid:*

I.	3.76	0.94	1.51	6.21	6.09
II.	4.05	1.01	1.05	6.11	„

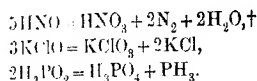
*(c) With sulphuric acid:*

I.	1.60	0.4	2.98	4.98	6.09
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NOTE.—The preparation and analysis of the samples of salts made use of in the experiments recorded in the above tables have been given at length in the previous memoirs on “Mercurous Hyponitrite” and “The Decomposition of Mercurous and Mercuric Hyponitrites by Heat” (this vol., pp. 1404, 1399).

*Discussion of Results.*

It will be seen that silver hyponitrite by reaction with the three mineral acids gives almost the theoretical yield of hyponitrous acid, which again breaks up into nitrous oxide, nitrogen, and nitric acid. According to Hantzsch and Kaufmann, ammonia and nitrous acid are among the decomposition products of hyponitrous acid, but under certain conditions they failed to detect either of these, obtaining instead traces of nitric acid, as, for instance, when they allowed hyponitrous acid to remain for twenty-four hours in contact with a few drops of hydrochloric acid. As these chemists contented themselves with proving, merely qualitatively, the existence of nitric acid, they erroneously concluded that it was derived from the oxidation of nitrous acid.\* In fact, the following three sets of reactions are strictly comparable:



When chlorine is passed into a hot concentrated solution of potassium hydroxide, the hypochlorite which may be taken to be potentially formed at once passes into compounds which are stable under the existing conditions. Hypophosphorous acid, again, is only stable at a low temperature; on being heated it gives rise to phosphoric acid and phosphine. In these two instances the oxidation does not stop short at the intermediate stage of chlorite or phosphite.

One remarkable feature is the behaviour of sulphuric acid, which invariably ensures a larger yield of nitrous oxide. It is evident that the presence of mineral acids has a specific directive influence in determining the course which the reaction follows.

As regards mercurous hyponitrite, the mechanism of the reaction is substantially the same as with its silver analogue. It is noteworthy, however, that the decomposition of this salt by means of sulphuric and nitric acids is never complete. In other words, silver hyponitrite is decomposed with equal readiness by both the oxygen and haloid acids, but the mercurous salt only by the latter.

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\* "Sontern Salpetersäure (durch Oxydation der Salpetrigen Säure entstanden)," *loc. cit.*, 333.

† Thum has shown that an aqueous solution of hyponitrous acid is directly oxidised to nitric acid by means of potassium permanganate. The three instances cited above are, however, those of autoxidation and reduction. \*

LXXXI.—*Contributions to the Chemistry of the Terpenes.*  
 Part II. *The Oxidation of Limonene with Chromyl Chloride.*

By GEORGE GERALD HENDERSON.

THE action of chromyl chloride on limonene is violent, but when moderated by dissolving each of these substances in a large quantity of carbon disulphide it results in the formation of a solid *additive product*,  $C_{10}H_{16} \cdot 2CrO_2Cl_2$ . This compound is decomposed by water with evolution of heat, chromic chloride passing into solution, and a brown, oily liquid, together with a quantity of resinous matter, separating. When the liquid oxidation product is purified by distillation in a current of steam, a further quantity of resinous matter is left in the distilling flask, and a yellow oil passes over. This oil contains at least three substances: an aldehyde, a ketone, and a smaller quantity of some chlorinated oxidation product, which, however, on account of its instability, could not be isolated. The *aldehyde*,  $C_{10}H_{14}O$ , which was separated by conversion into the crystalline *compound* which it forms with sodium hydrogen sulphite, is a colourless, oily liquid with a strong odour. It is unsaturated, and on exposure to air it undergoes oxidation to a crystalline *acid*,  $C_{10}H_{14}O_2$ . The *silver* salt of the acid crystallises from water, in which it is sparingly soluble, in white needles. When the aldehyde is oxidised by heating with dilute nitric acid, it does not yield the acid  $C_{10}H_{14}O_2$ , but is converted into *p*-toluic acid. *p*-Toluic acid is also the principal product obtained when the aldehyde is oxidised with a dilute solution of potassium permanganate. The *semicarbazone* of the aldehyde crystallises from methyl alcohol in glistening leaflets. The *ketone*,  $C_{10}H_{16}O$ , which is the main constituent of the oxidation product, is an oily liquid with a faint yellow colour and a characteristic odour. It is unsaturated. The *semicarbazone* of the ketone crystallises from methyl alcohol in lustrous prisms, which contain one molecule of methyl alcohol, and which effloresce quickly when exposed to air, yielding a white powder. When heated with ammonium formate, the ketone is converted into the formyl derivative of an *amine*,  $C_9H_{13} \cdot NH_2$ . The amine is a colourless liquid with a disagreeable odour, and is almost insoluble in water. Its hydrochloride and sulphate are deliquescent, and are extremely easily soluble in water or alcohol; its *platinichloride*, which is sparingly soluble, forms brownish-yellow crystals.

Unfortunately, the yields are very small, and the quantities of the aldehyde and the ketone hitherto obtained have not permitted of a full examination of these substances. However, enough has been

done to show that, under suitable conditions, limonene behaves with chromyl chloride similarly to pinene (Trans., 1903, 83, 1299), at least to the extent that the solid additive compound which is formed from each of the hydrocarbons is decomposed by water with the formation in each case of an aldehyde, a ketone, and a product containing chlorine as well as oxygen. It is intended to continue the investigation of these substances.

#### EXPERIMENTAL.

##### *Oxidation of the Hydrocarbon.*

For the first oxidation experiments, *d*-limonene (dipentene) was prepared from oil of bitter orange. The oil was agitated with aqueous sodium carbonate and then with water, dried, and distilled. The portion which distilled at 174–178° was mixed with half its volume of glacial acetic acid, and dry hydrogen chloride was passed slowly over the mixture, which was kept cool with ice, and was shaken at intervals. After some days the mixture solidified; water was added, and the crystalline dipentene dihydrochloride which separated was collected and purified by solution in a small quantity of alcohol and precipitation with water. A mixture of the dihydrochloride with an equal weight of anhydrous sodium acetate and twice its weight of glacial acetic acid was boiled under a reflux condenser for half an hour, and the liberated hydrocarbon was then distilled off with a current of steam. The impure hydrocarbon was collected, boiled for some time under a reflux condenser with dilute aqueous potassium hydroxide, distilled over with steam, dried, and fractionated. Almost the whole of it distilled at 175–176°. In later experiments, *d*-limonene, also prepared from oil of bitter orange, was used. The oil was shaken with a solution of sodium carbonate, distilled in a current of steam, collected, dried, and finally fractionated with the aid of a "pear" still-head. In this way, a large fraction was obtained which boiled constantly at 175–176°.

The oxidation of the limonene was effected in a similar manner to that of pinene (*loc. cit.*). A 10 per cent. solution of chromyl chloride (2 mols.) in pure, dry carbon disulphide was added slowly to a similar solution of limonene (1 mol.), the flask containing the latter being cooled with ice-water and constantly shaken. The dark brown precipitate which slowly settled was collected, washed with carbon disulphide, and while still mixed with some of that liquid, with which it forms a pasty mass, thrown in small quantities at a time into ice-cold water, the mixture being well shaken after each addition. A little sulphurous acid was added to the water, in order to reduce any chromic acid which might be formed during the decomposition of the additive product. When the action was completed, the oxidation

product was extracted by means of carbon disulphide; a considerable quantity of a brown, resinous substance was left undissolved. The carbon disulphide solution was well washed with water and dried with calcium chloride, and, after removal of the solvent, the brown, oily residue was purified by distillation with steam. More resinous matter was left in the distilling flask, and the clear, yellow oil which passed over was separated from the water by means of ether.

The *additive compound*,  $C_{10}H_{16} \cdot 2CrO_2Cl_2$ , which is formed by the action of chromyl chloride on limonene, is, when dry, a powder of a greyish-brown colour, which on heating evolves hydrogen chloride. On exposure to the air, it quickly begins to absorb moisture and to decompose, and it reacts at once with water, yielding a viscous, brown liquid insoluble in water, a quantity of resinous matter insoluble in carbon disulphide, and a solution containing chromic chloride and usually a little chromic acid.

#### *Preparation of the Aldehyde, $C_{10}H_{14}O$ .*

The ethereal solution of the purified oxidation product was concentrated to small bulk, and shaken with a freshly-prepared saturated solution of sodium hydrogen sulphite. The additive compound,  $C_{10}H_{14}O \cdot NaHSO_3$ , which slowly separated in small, shining crystals, was collected and washed with alcohol and with ether, and the ethereal solution of the residual oil was again shaken with a fresh quantity of the bisulphite solution. This process was repeated until no more crystals formed, even after a period of several days, when it was considered that the aldehyde was completely removed from the original solution. The purified bisulphite compound was mixed with aqueous sodium carbonate, and the liberated aldehyde was distilled off in a current of steam and extracted from the distillate with ether. The ethereal solution was dried with calcium chloride, and, after removal of the ether, the aldehyde was purified by fractional distillation under diminished pressure in a current of dry carbon dioxide. From the filtrates obtained during the preparation and purification of the bisulphite compound, which is fairly readily soluble in water and in alcohol, a further quantity of less pure aldehyde was obtained, after removal of the ether and alcohol, by addition of sodium carbonate and distillation with steam.

The *aldehyde* thus obtained from limonene is an almost colourless, oily liquid with a strong, peculiar odour. It is practically insoluble in water, but dissolves freely in alcohol or ether; it boils at  $221^{\circ}$ – $222^{\circ}$  under a pressure of 755 mm. It shows the characteristic reactions of aldehydes, giving a crystalline bisulphite compound, reducing ammoniacal solutions of silver salts, restoring the colour to magenta



decolorised with sulphurous acid, and forming a crystalline semicarbazone. It is unsaturated, as it at once unites with bromine dissolved in dry chloroform, yielding an unstable additive compound, which quickly decomposes and evolves hydrogen bromide. It undergoes oxidation when exposed to the air. The results of several analyses pointed to the formula  $C_{10}H_{14}O$ .

The semicarbazone of the aldehyde,  $C_{10}H_{11}N \cdot NH \cdot CO \cdot NH_2$ , prepared in the usual manner, crystallises in small, lustrous leaflets which melt at  $156-157^\circ$ . It is fairly readily soluble in cold, easily so in hot methyl alcohol:

0.1021 gave 17.8 c.c. of nitrogen at  $19^\circ$  and 765 mm.  $N = 20.6$ .

0.2020 " 36 c.c. " "  $20^\circ$  " 765 mm.  $N = 20.7$ .

$C_{10}H_{17}ON_3$  requires  $N = 20.3$  per cent.

#### *Preparation of the Acid, $C_{10}H_{14}O_2$ .*

When exposed to the air, the aldehyde was gradually converted through oxidation into a soft, semicrystalline mass. This was warmed with a solution of sodium carbonate, and the solution was extracted several times with ether, in order to remove unchanged aldehyde, and then acidified. The acid, which separated in an oily state, was extracted by means of ether, and, after removal of the ether, was purified by repeated crystallisations from slightly diluted methyl alcohol. The process of purification was troublesome on account of the tendency of the acid to separate in an oily state, but it was finally obtained in small, colourless crystals which melt at  $172^\circ$ . It is very readily soluble in alcohol and in ether, but practically insoluble in water, and it is hardly, if at all, volatile in a current of steam.

The quantity of the purified acid available being too small for analysis, it was converted into the silver salt,  $C_{10}H_{13}O_2Ag$ . This salt was precipitated from a solution of the ammonium salt as a white, crystalline powder, and was purified by crystallisation from water, from which it separates in small, white prisms. It is fairly readily soluble in hot, but sparingly so in cold, water:

0.3278 gave 0.1292 Ag.  $Ag = 39.4$ .

$C_{10}H_{13}O_2Ag$  requires  $Ag = 39.6$  per cent.

When the aldehyde is boiled for some time with dilute nitric acid, it is oxidised to an acid different from that just described. This acid, after purification by crystallisation from light petroleum, melts at  $178^\circ$ . It separates from aqueous solution in small, colourless needles. It dissolves very easily in alcohol or ether, fairly readily in hot water, and very sparingly in hot light petroleum, and it volatilises, although rather slowly, in a current of steam. It is saturated, since it does not reduce potassium permanganate and does not form an additive com-

pound with bromine. In all these properties, this acid corresponds very closely with *p*-toluic acid, and its identity with the latter was established by analysis of the acid itself and of its silver salt:

0.1592 gave 0.4114  $\text{CO}_2$  and 0.0886  $\text{H}_2\text{O}$ .  $\text{C} = 70.5$ ;  $\text{H} = 6.2$ .

$\text{C}_9\text{H}_8\text{O}_2$  requires  $\text{C} = 70.6$ ;  $\text{H} = 5.9$  per cent.

The silver salt was obtained as a white, crystalline precipitate, which was thoroughly washed and dried:

0.3592 gave 0.1770  $\text{Ag}$ .  $\text{Ag} = 44.3$ .

$\text{C}_9\text{H}_7\text{O}_2 \text{ Ag}$  requires  $\text{Ag} = 44.4$  per cent.

If the aldehyde is oxidised with a 2 per cent. solution of potassium permanganate, the chief product, even in the cold, is again *p*-toluic acid, but if a considerably more dilute solution of the reagent is employed, some of the acid,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ , is also obtained. It is evident that this acid is easily converted into *p*-toluic acid by oxidation.

#### *Preparation of the Ketone, $\text{C}_9\text{H}_{12}\text{O}$ .*

The ethereal solution of the oxidation products of limonene, from which the aldehyde had been removed as described above, was washed with a solution of sodium carbonate and then with water, dried, and heated until the ether was removed. Preliminary examination of the oily residue showed that, in addition to the ketone, it contained a smaller quantity of a chlorinated substance. It was found impossible to isolate the latter, because treatment of the mixture with solvents did not effect a separation, whilst on distillation, even when the pressure was reduced to 15 mm., it began to decompose with liberation of water and hydrogen chloride. Since the presence of this chlorinated compound rendered the purification of the ketone difficult, the mixture of substances was treated with alcoholic potash in sufficient quantity to decompose it, and, after removal of the precipitate of potassium chloride, which was formed almost at once, the filtrate was mixed with water and extracted several times with ether. The ethereal solution was separated, well washed with water, and dried over calcium chloride, the ether was removed, and the residual oil was distilled at 15 mm. in a current of dry carbon dioxide. After repeated distillations, a large fraction, which boiled constantly at  $112-113^\circ$ , was obtained.

The *ketone* is an oily liquid with a faint yellow colour and a camphor-like odour. It dissolves readily in the usual organic solvents, but is insoluble in water. It does not unite with sodium hydrogen sulphite, but forms a crystalline semicarbazone. It is unsaturated, combining at once with bromine in chloroform solution, but the additive product which is formed is unstable, and begins to evolve

hydrogen bromide almost at once. The boiling point of the ketone is  $112^{\circ}$ – $113^{\circ}$  under a pressure of 15 mm.:

0.1090 gave 0.3155  $\text{CO}_2$  and 0.0930  $\text{H}_2\text{O}$ .  $\text{C} = 79$ ;  $\text{H} = 9.5$ .

0.1366 „ 0.3950  $\text{CO}_2$  „ 0.1150  $\text{H}_2\text{O}$ .  $\text{C} = 78.9$ ;  $\text{H} = 9.3$ .

$\text{C}_{10}\text{H}_{12}\text{O}$  requires  $\text{C} = 79.4$ ;  $\text{H} = 8.8$  per cent.

The semicarbazone of the ketone,  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$ , was prepared in the usual way and purified by crystallisation from methyl alcohol. It separates from that solvent in clusters of lustrous, transparent needles, but the crystals, when exposed to the air, rapidly become opaque, and are then easily crushed to a white powder. Analysis showed that the needle-shaped crystals contain one molecule of methyl alcohol of crystallisation, which is quickly lost at the ordinary temperature. After being heated to  $100^{\circ}$  in order to expel all the methyl alcohol, the semicarbazone melts at  $205^{\circ}$ . It is only moderately soluble in hot, and very sparingly so in cold, methyl alcohol:

0.1378 gave 27 cc. nitrogen at  $20^{\circ}$  and 752 mm.  $\text{N} = 22.2$ .

0.1449 „ 27.3 cc. „ „  $19^{\circ}$  „ 758 mm.  $\text{N} = 22.2$ .

$\text{C}_{10}\text{H}_{12}\text{ON}_3$  requires  $\text{N} = 21.8$  per cent.

In order to determine the proportion of methyl alcohol of crystallisation, the crystals were quickly pressed in bibulous paper, weighed, and heated at  $105^{\circ}$ :

0.8555 lost 0.1236.  $\text{MeOH} = 14.4$ .

$\text{C}_{10}\text{H}_{11}\text{ON}_3\text{C}_2\text{H}_5\text{OH}$  requires  $\text{MeOH} = 14.3$  per cent.

#### *Preparation of the Amine, $\text{C}_{10}\text{H}_{13}\text{NH}_2$ .*

The ketone, mixed with twice its weight of dry ammonium formate, was heated at  $165^{\circ}$  in a sealed tube for twelve hours. The contents of the tube were treated with ether, the solution was filtered, the ether was removed, and the residue, consisting mainly of the formyl derivative of the amine, was hydrolysed by heating for about twelve hours with excess of alcoholic potash under a reflux condenser. Water was then added, the moisture was shaken several times with ether, and the ethereal solution was washed with water and then shaken with dilute hydrochloric acid. The solution of the hydrochloride of the amine was mixed with excess of potassium hydroxide and the liberated amine was distilled off with a current of steam. The distillate was neutralised with hydrochloric acid, and, after evaporation of the solution to dryness on the water-bath, the hydrochloride of the amine was obtained as a deliquescent, crystalline mass. It is extremely easily soluble in water and in alcohol, and from alcoholic solution is precipitated by ether in the form of a syrupy liquid which showed no signs of becoming crystalline even after long

standing under ether. The sulphate and the nitrate of the amine are also easily soluble, deliquescent substances, but the platinumchloride is very sparingly soluble in water.

The amine, of which the quantity obtained was unfortunately very small, is a colourless liquid with a disagreeable odour and an alkaline reaction. It is almost insoluble in water, but readily soluble in alcohol or ether, and it volatilises easily in steam. The platinumchloride of the amine crystallises in small, brownish-yellow needles, and is sparingly soluble in hot water:

0.1032 gave 0.0290 Pt. Pt = 28.1.

$(C_9H_{13}NH_2)_2PtCl_2$  requires Pt = 28.5 per cent.

I am indebted to Mr. W. T. Munro and to Mr. J. A. Campbell, A.I.C., for assistance with part of this work, and to the Committee of the Carnegie Trust for a grant in defrayal of the expense.

CHEMISTRY DEPARTMENT,  
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

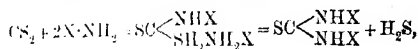
## CLXXXII.—*Studies in the Camphane Series. Part XXIV. Camphoryldithiocarbamic Acid and Camphorylthiocarbimide.*

By MARTIN ONSLOW FORSTER and THOMAS JACKSON.

WHEN bornylcarbimide was obtained by the action of nitrous acid on bornylcarbamide (Forster and Attwell, Trans., 1904, 85, 1188), it was hoped that the resolution of racemic alcohols might be effected by converting these into a mixture of carbamates, separable by fractional crystallisation, but the comparative indifference of bornylcarbimide towards alcohols precludes its application to this problem. Since then, however, Pickard and Littlebury (Trans., 1906, 89, 467) have accomplished the division of racemic  $\alpha$ -phenyl- $\alpha'$ -1-hydroxyphenylethane by means of *l*-menthylcarbimide, and it is probable that camphorylcarbimide (Forster and Fierz, Trans., 1905, 87, 110) could be used for a similar purpose, as it has the property of yielding acetanilides with simple alcohols. The production of these carbimides, however, presents certain difficulties, and it seemed desirable to ascertain whether an optically active thiocarbimide could not be prepared more readily, and applied for the purpose indicated. Unsuccessful experiments with this object had been made with bornyl-

amine (Forster and Attwell, *loc. cit.*), and we therefore proceeded to study the possibilities of aminocamphor in the hope that camphorylthiocarbamide might be made to yield camphoryl mustard oil by a process analogous to the well-known transformation of diphenylthiocarbamide into phenylthiocarbimide.

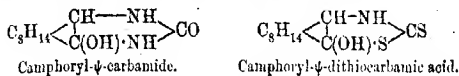
On heating an ethereal solution of aminocamphor with carbon disulphide, however, we were surprised to find that hydrogen sulphide is not set free, owing to the remarkable stability of camphoryldithiocarbamic acid,  $C_{10}H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH} \cdot \text{CS} \cdot \text{SH} \\ \text{CO} \end{smallmatrix}$ . The usual result of treating an aliphatic amine with carbon disulphide is the formation of alkylamine alkylthiocarbamate, which gradually breaks up into dialkylthiocarbamide and hydrogen sulphide,



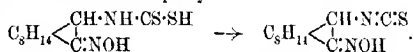
and this is the course which bornylamine follows. In the aromatic series, the intermediate stage is not observed, aniline phenylthiocarbamate, for instance, losing hydrogen sulphide too quickly to permit of its being isolated, although Losanitsch (*Ber.*, 1891, 24, 3921; 1907, 40, 2970) has shown that if the action of carbon disulphide on aniline is conducted in presence of ammonia, elimination of hydrogen sulphide may be arrested, and the ammonium salt of phenylthiocarbamic acid produced. The literature shows that a variety of aliphatic amines have been treated with carbon disulphide, but in no case, so far as we have been able to ascertain, has the dithiocarbamic acid been isolated; the aromatic representatives, also, would appear to be most unstable, phenylthiocarbamic acid, for example, having been described as changing immediately into thiocarbamide, hydrogen sulphide, and carbon disulphide (Rathke, *Ber.*, 1878, 11, 958).

The stability of camphoryldithiocarbamic acid appears therefore to be unique, and the nearest approach to its properties is furnished by phenylthiocarbazonic acid,  $C_6H_5 \cdot NH \cdot NH \cdot CS \cdot SH$ , the phenylhydrazine salt of which was described by E. Fischer (*Annalen*, 1878, 190, 115). Busch records a definite melting point for the free acid (*Ber.*, 1895, 28, 2659), but Busch and Ridder (*Ber.*, 1897, 30, 845) describe the substance as somewhat unstable, in part changing into phenylhydrazine phenylthiocarbazinate, whilst the remainder undergoes a more profound decomposition and becomes black. No change of this character has been observed in connexion with camphoryldithiocarbamic acid, a colourless, crystalline specimen of which has now been exposed to diffused light during more than six months without altering in appearance or developing any odour. In speculating as to

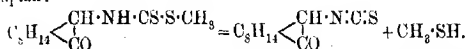
the cause of this stability, we were naturally led to ascribe it to the neighbourhood of the carbonyl group, and, in view of the isomerism observed in connexion with camphorylcarbamide (Forster and Fierz, *loc. cit.*), considered the possibility of representing it as a pseudo-modification of the normal dithiocarbamic acid:



For several reasons, however, this explanation appears most unlikely. In the first place, the substance is a strong acid, and also differs from camphoryl- $\psi$ -carbamide in its failure to yield a nitroso-derivative. Furthermore, the oxime of camphoryldithiocarbamic acid, prepared by the action of carbon disulphide on aminocamphoroxime, although capable of a separate existence, readily loses hydrogen sulphide, passing into the oxime of camphorylthiocarbamide:



Finally, the methyl ester of camphoryldithiocarbamic acid, a colourless substance melting sharply at  $147^\circ$  without liberating gas, breaks up at about  $170^\circ$ , yielding camphorylthiocarbimide and methyl mercaptan:

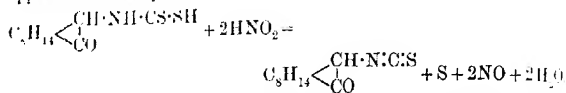


We conclude therefore that the stability of camphoryldithiocarbamic acid is merely another manifestation of the remarkable influence exerted by the carbonyl radicle upon the functions of a group attached to the neighbouring carbon atom, and in this association the behaviour of other aminoketones towards carbon disulphide might repay investigation.

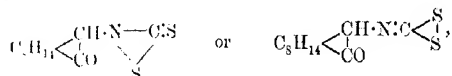
Another interesting distinction from the dithiocarbamic acids, derivatives of which have been described hitherto, is to be found in the power displayed by the camphoryl derivative to yield a benzoyl compound. Numerous alkyl esters of dithiocarbamic acids have been prepared, even from the unstable compounds of the aliphatic and aromatic series, but the action of benzoyl chloride on the acids has either not been studied, or has led to negative results. In the case of phenyldithiocarbamic acid, Busch and Becker, who described definite ethyl and benzyl esters (*J. pr. Chem.*, 1899, [ii], 60, 217), state that the benzoyl derivative cannot be isolated, as it loses water immediately, and gives diphenylisodithiodiazolone,  $\text{C}_6\text{H}_5 \cdot \text{N} \begin{array}{c} \text{N} \text{---} \text{CS} \\ \diagdown \quad \diagup \\ \text{C}(\text{C}_6\text{H}_5) \cdot \text{S} \end{array}$ , along with *s*-dibenzoylphenylhydrazine. From camphoryldithiocarbamic acid and benzoyl chloride in ether, however, we have obtained a well-

defined benzoyl derivative which may be recrystallised; nevertheless, it is easily decomposed into camphorylthiocarbimide and, presumably, thiobenzoic acid, and the mustard oil alone is isolated if the benzoylation of camphoryldithiocarbamic acid is attempted under ordinary conditions in presence of alkali.

The action of nitrous acid on the dithiocarbamic acid, although leading ultimately to the mustard oil, is not quite so simple as would appear from the equation:



There is evidence that an intermediate product of oxidation is first formed without loss of sulphur, because an ethereal solution of camphoryldithiocarbamic acid, when mixed with amyl nitrite, develops a dark brown coloration, and deposits colourless prisms consisting of the substance:

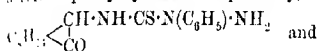


unmixed with sulphur; the product may be recrystallised from cold solvents, but, if the temperature is raised, breaks up into camphorylthiocarbimide and sulphur. It may be noted as a curious point that, whilst the specific rotatory power of the oxidation product is  $[\alpha]_D^{20} 102^\circ$ , the thiocarbimide is levorotatory, having  $[\alpha]_D -114^\circ$ .

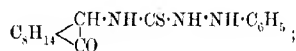
The investigation of camphoryldithiocarbamic acid has brought to light a variety of methods by which the mustard oil may be obtained from it. Two of these have already been mentioned, and a third is the normal decomposition of the mercuric salt when warmed with alcoholic ammonia; a less usual one consists in mixing pyridine solutions of the dithiocarbamic acid and benzoyl chloride, and in attempting to prepare the benzenesulphonic derivative it was found that the thiocarbimide is produced almost quantitatively when an alkaline solution of the dithiocarbamate is agitated with benzenesulphonic chloride. A sixth process depends on the behaviour of camphorylthiocarbimide towards nitrous acid, which does not give rise to a nitro-o-derivative, thus classifying the thiocarbimide with camphorylthiocarbimide instead of with the pseudo-modification.

It does not appear probable that the mustard oil will prove serviceable in the task of resolving racemic alcohols, its reaction with the hydroxyl group being sluggish; methyl camphorylthiocarbamate was obtained when the factors were heated at  $150^\circ$  during five hours. The behaviour of the thiocarbimide towards phenylhydrazine is

interesting, however, and three definite products have been isolated, two of which have the empirical formula of a camphorylphenylthiosemicarbazide, whilst the third is evidently an internal anhydride or phenylhydrazone. The work of A. E. Dixon (*Trans.*, 1892, **61**, 1012) and of Marckwald (*Ber.*, 1892, **25**, 3098; 1899, **32**, 1081) has shown that many of the thiosemicarbazides produced from aromatic thiocarbimides and hydrazines exist in two modifications, which Busch and Holzmann (*Ber.*, 1901, **34**, 320) have proved to be structurally distinct (compare also Busch, Opfermann, and Walther, *Ber.*, 1904, **37**, 2318). Owing to lack of material, our examination of the camphorylphenylthiosemicarbazides has not been so complete as that of the authors mentioned, but we believe them to be  $\alpha$ - and  $\beta$ -derivatives of phenylhydrazine respectively, as represented by the formulæ:

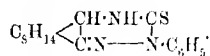


M. p. 183°.



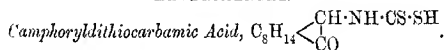
M. p. 143°.

the modification melting at 183° readily passes into the anhydride, which most probably has the constitution:



Although the two thiosemicarbazides have almost the same specific rotatory power, the colours which they develop with sulphuric acid, copper acetate, ferric chloride, bleaching powder, nickel acetate, and ammoniacal silver oxide render it a simple matter to distinguish between the isomeric forms, and to differentiate these from the anhydride. We have not been able to transform the  $\alpha$ -derivative into the isomeride by boiling the alcoholic solution with a small quantity of hydrochloric acid (compare Marckwald, *loc. cit.*), because this treatment gives rise to the anhydride, but we have shown that, under the same conditions, the  $\beta$ -modification is not converted into the less fusible form.

#### EXPERIMENTAL.



One hundred grams of isonitrosocamphor were reduced in alkaline solution with zinc dust, and the aminocamphor, after extraction with ether, was converted into the hydrochloride and reprecipitated by alkali; the solution in ether was then dried with solid potassium hydroxide, immersed in cold water, and slowly mixed with 48 grams of carbon disulphide. Heat was developed, and when action was complete the



solvent was evaporated until about 200 c.c. of liquid remained; as this product cooled, it solidified to a crystalline cake which, when drained on earthenware, weighed 110 grams instead of 134. The substance was recrystallised from methyl alcohol, forming glistening, hexagonal plates which melt and decompose at  $128^{\circ}$ :

0.2337 gave 12.1 c.c. of nitrogen at  $18^{\circ}$  and 755.5 mm.  $N = 5.91$ .

0.1603 " 0.1939  $\text{BaSO}_4$ .  $S = 26.50$ .

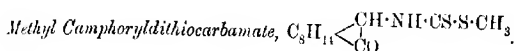
$\text{C}_{11}\text{H}_{17}\text{ONS}_2$  requires  $N = 5.77$ ;  $S = 26.33$  per cent.

The yield of dithiocarbamic acid is not impaired when the ethereal solution of aminocamphor is heated with carbon disulphide in a reflux apparatus during many hours, but, if solvents of higher boiling point are used, hydrogen sulphide is liberated slowly, and the normal change into disubstituted thiocarbamide takes place. In recrystallising the substance, therefore, it is advisable to proceed as rapidly as possible, and to deal with moderate quantities; although cold chloroform dissolves it sparingly, an attempt to recrystallise 50 grams from this medium failed, owing to the necessity of boiling it with the solid for some minutes, the filtered liquid depositing no crystals on cooling, and yielding a gummy residue from which dicamphorylthiocarbamide alone was obtainable. Cold acetone or ether and hot methyl and ethyl alcohols dissolve the dithiocarbamic acid freely, forming supersaturated solutions; hot benzene dissolves it sparingly, and it is practically insoluble in boiling light petroleum. The substance is a pronounced acid, dissolving in sodium carbonate and cold dilute caustic alkali without change, but hot alkalis transform it into dicamphorylthiocarbamide.

A solution containing 0.2614 gram in 25 c.c. of acetone gave  $\alpha_D 0.27$  in a 2 dm. tube, whence  $[\alpha]_D 21.5^{\circ}$ ; on exposing this liquid to light during several days, it became yellow and levorotatory to the extent of  $\alpha_D 0.15$ , indicating transformation into camphorylthiocarbamide (see below). A 2 per cent. solution of the dithiocarbamic acid in potassium hydroxide is inactive, and remains so when heated at  $60^{\circ}$  during several days, when the pale yellow liquid gradually becomes green without depositing dicamphorylthiocarbamide, although this is precipitated on acidification. An alcoholic solution giving  $\alpha_D 18'$  when freshly prepared increased in optical activity to  $\alpha_D 120'$  after three months, sulphur separating in well-defined crystals. An ethereal solution of the acid develops a deep brown coloration with ferric chloride, but there is no change when sodium nitroprusside is added to a solution in alcohol or dilute ammonia.

*Behaviour towards Metallic Salts.*—When alcoholic copper acetate is added to a moderately concentrated solution of camphoryldithiocarbamic acid in the same solvent, a deep brown coloration is developed

but there is no precipitate until copper is in excess, when a pale brown derivative appears; on warming this compound in the liquid, it becomes faintly yellow and highly insoluble. Alcoholic silver nitrate develops a deep yellow colour, the liquid remaining clear, but on adding a few drops of alcoholic ammonia a pale brown precipitate is formed, sparingly soluble in boiling alcohol; excess of alcoholic ammonia dissolves this material, and the solution may be boiled without precipitating silver sulphide. Lead acetate forms a bulky, pale yellow salt, which, when boiled with alcohol, deposits lead sulphide in the form of a mirror. A solution of mercuric chloride in alcohol yields a bulky, snow-white precipitate which does not change in appearance when the liquid is boiled. If the solution of camphoryldithiocarbamic acid is faintly ammoniacal, however, the precipitate with alcoholic mercuric chloride is yellow, and quickly becomes black on boiling, whilst the filtered liquid yields crystals of camphoryldithiocarbimide.



Camphoryldithiocarbamic acid combines with methyl iodide very readily, hydrogen iodide being eliminated when the two materials are warmed together. Twenty grams of the acid were dissolved in a solution methyl alcohol containing 2 grams of sodium, and treated with 15 grams of methyl iodide; the deep yellow colour faded, and, after a few minutes on the steam-bath, water was added, the crystalline precipitate being then filtered quickly and washed with cold water. While the substance remained moist, it retained the offensive odour of methyl mercaptan, but this was gradually lost in the desiccator, and on recrystallising the dry material from boiling petroleum, in which it dissolves readily, silky, centimetre-long needles were obtained quite odourless, and melting at  $147^\circ$  without evolving gas:

0.2005 gave 9.6 c.c. of nitrogen at  $16^\circ$  and 765 mm.  $N = 5.62$ .

0.0957 " 0.1730  $\text{BaSO}_4$ .  $S = 24.78$

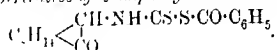
$C_{12}H_{19}ONS_2$  requires  $N = 5.45$ ;  $S = 24.90$  per cent.

A solution containing 1.0450 grams in 25 c.c. of chloroform gave  $n_D^{20} 1.435$  in a 2-cm. tube, whence  $[\alpha]_D 114.6^\circ$ . The ester is freely soluble in chloroform, benzene, acetone, ether, or ethyl acetate, less readily in methyl and ethyl alcohols; it is very sparingly soluble in cold petroleum, and an ethereal solution gives no colour with ferric chloride.

*Decomposition by Heat.*—When warmed with water, the odour of methyl mercaptan quickly becomes perceptible, followed by the pungent vapour of camphoryldithiocarbimide rising with the steam.

Five grams of the dry ester were mixed with clean, white sand in a small distilling flask connected with a double U-tube immersed in a freezing mixture, the apparatus having been carefully dried, and closed by a tube of calcium chloride. The flask was heated in an oil-bath at 170° during two hours, when approximately 1 c.c. of methyl mercaptan collected in the receiver; this product was identified by conversion into the mercury compound, which melted at 177° after crystallisation from alcohol. The residue in the flask was recognised as camphoryldithiocarbimide.

*Benzoyl Derivative of Camphoryldithiocarbamic Acid,*



On attempting to benzoylate camphoryldithiocarbamic acid under the familiar conditions of the Schotten-Baumann process, it was found that camphoryldithiocarbimide is the main product. Experiments in which benzoyl chloride acted on the acid dissolved in pyridine gave distinct evidence of the formation of a benzoyl derivative, for, on dissolving the well-washed product in alcohol, ethyl benzoate was recognisable in the liquid, although it was the thiocarbimide which crystallised on cooling. Even when the material arising by benzoylation in pyridine is dried as quickly as possible without heating, and recrystallised from petroleum to exclude water, the benzoyl derivative is mixed with camphoryldithiocarbimide, but an individual substance may be obtained by employing ether as a medium.

Ten grams of camphoryldithiocarbamic acid were dissolved in 100 c.c. of dried ether and mixed with 6 grams of benzoyl chloride; on evaporating the solvent in a current of dry air, clusters of yellow needles separated, and on recrystallisation from warm petroleum, in which it is moderately soluble, the benzoyl derivative was obtained in long, colourless, silky needles melting at 105°:

0.2690 gave 9.2 c.c. of nitrogen at 20° and 762.5 mm.  $N = 3.92$ .

0.0994 .. 0.1357  $\text{BaSO}_4$ .  $S = 18.74$ .

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{NS}_2$  requires  $N = 4.03$ ;  $S = 18.44$  per cent.

A solution containing 0.2865 gram in 25 c.c. of chloroform gave  $\alpha_D^{20} 1.12'$  in a 2-dm. tube, whence  $[\alpha]_D^{20} 52.3^\circ$ . The benzoyl derivative is freely soluble in chloroform, benzene, acetone, and ethyl acetate, less readily in methyl and ethyl alcohols, solutions in these media depositing camphoryldithiocarbimide on cooling; even when petroleum is employed, there is danger of decomposing the benzoyl derivative, and it is only by operating with small quantities, and cooling the liquid as rapidly as possible, that a specimen of the benzoyl derivative unmixed with thiocarbimide can be obtained.

*Action of Amyl Nitrite on Camphoryldithiocarbamic Acid.*

In preparing camphoryldithiocarbimide by the action of nitrous acid on camphoryldithiocarbamic acid (see below), various indications suggested the formation of an intermediate compound which passed into the mustard oil with loss of sulphur, and this material was ultimately isolated in the following manner.

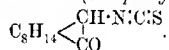
Camphoryldithiocarbamic acid was dissolved in dry ether and mixed with an equal weight of amyl nitrite, which immediately developed a dark reddish-brown coloration, followed by continuous evolution of red gas; as the effervescence proceeded, the colour of the liquid gradually disappeared and colourless prisms separated. Attempts to recrystallise this material led at first to the thiocarbimide with elimination of sulphur, but on dissolving the substance in chloroform and adding petroleum, colourless crystals were obtained which become yellow at about 110°, melting and decomposing at 116°:

0.3287 gave 16.4 c.c. of nitrogen at 20° and 755 mm.  $N = 5.67$ .

0.0956 " 0.1776 BaSO<sub>4</sub>.  $S = 26.05$ .

$C_{11}H_{15}ONS_2$  requires  $N = 5.81$ ;  $S = 26.55$  per cent.

The formulae  $C_{11}H_{15}ONS_2$  and  $C_{22}H_{32}O_2N_2S_4$ , being indistinguishable by analysis, determinations of molecular weight were made in benzene and in phenol. In the former solvent, the results were abnormal, averaging about 700, but in phenol an average of 227 was obtained, corresponding with the simpler formula  $C_{11}H_{15}ONS_2$ , which requires 241, whilst  $C_{22}H_{32}O_2N_2S_4$  amounts to 484. A solution containing 0.5972 gram in 25 c.c. of chloroform gave  $\alpha_D^{20} 30'$  in a 2-dm. tube, whence  $[\alpha]_D^{20} 101.7^\circ$ . The substance is freely soluble in chloroform or benzene, but dissolves less readily in acetone or ethyl acetate; methyl and ethyl alcohols dissolve it sparingly, and it is practically insoluble in light petroleum.

*Camphoryldithiocarbimide (Camphoryl Mustard Oil),*

Twenty grams of camphoryldithiocarbamic acid were dissolved in 50 c.c. of pyridine, cooled with ice, and mixed with 12 grams of benzoyl chloride, also dissolved in pyridine; the temperature rose, and pyridine hydrochloride separated. After ten minutes, ice-water was added, the oily precipitate quickly becoming solid; this was drained on earthenware and boiled with alcohol containing a small proportion of water, the hot liquid depositing 17 grams of thiocarbimide as it cooled. The following alternative method was also satisfactory.

Twenty c.c. of concentrated hydrochloric acid were added to 10 grams of camphoryldithiocarbamic acid dissolved in 200 c.c. of absolute alcohol, the ice-cold liquid being then treated with 5 grams of sodium nitrite in the minimum quantity of water. The first portions of the salt developed an intense brown coloration in the liquid, and a colourless precipitate was formed; this was collected after two hours, digested with warm absolute alcohol, and the solution filtered from sulphur and sodium chloride. On adding water, the thiocarbimide was precipitated, and, when recrystallised from a small quantity of hot absolute alcohol, separated in long, lustrous prisms which melt at 106.5°:

0.1804 gave 10.4 c.c. of nitrogen at 20° and 771.5 mm.  $N = 6.70$ .

0.1068 " 0.1174  $\text{BaSO}_4$ .  $S = 15.07$ .

$\text{C}_{11}\text{H}_{15}\text{ONS}$  requires  $N = 6.70$ ;  $S = 15.31$  per cent.

A solution containing 0.2263 gram in 25 c.c. of absolute alcohol gave  $a_D = 2.4$  in a 2-dm. tube, whence  $[\alpha]_D = 114.1^\circ$ ; after several weeks, the activity of the solution almost disappeared, becoming stationary at  $a_D = 0.5$ . The mustard oil is readily soluble in benzene, and moderately so in alcohol; petroleum dissolves it readily when boiled, depositing lustrous, silky needles on cooling. It is insoluble in water, and the vapour in steam has a pungent odour which recalls that of camphorylecarbimide rather than phenyl mustard oil; boiling water and alkalis convert it slowly into dicamphorylthiocarbamide. Although sluggish in its action on water and alcohols, it reacts readily with ammonia and amines, yielding the following typical derivatives.

*Camphorylthiocarbamide*,  $\text{C}_8\text{H}_{14}\text{C}(=\text{O})\text{CH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , prepared by

passing dry ammonia into a solution of the thiocarbimide in chloroform, separated on adding petroleum as an oil which rapidly solidified; when recrystallised from boiling water, it formed slender laminae with silky lustre, and melted at 180°, evolving gas:

0.278 gave 22.1 c.c. of nitrogen at 15.5° and 764 mm.  $N = 12.49$ .

$\text{C}_{11}\text{H}_{15}\text{ON}_2\text{S}$  requires  $N = 12.41$  per cent.

A solution containing 0.2640 gram in 25 c.c. of chloroform gave  $a_D = 0.57$  in a 2-dm. tube, whence  $[\alpha]_D = 44.9^\circ$ . The substance dissolves readily in cold alcohol, and is moderately soluble in boiling water and in hot benzene, but is practically insoluble in petroleum. With nitrous acid, it gives the thiocarbimide, behaving in this respect like camphorylecarbimide (Trans., 1905, 87, 118).

*Camphorylpyridylthiocarbamide*,  $\text{C}_8\text{H}_{14}\text{C}(=\text{O})\text{CH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NC}_5\text{H}_5$ , was

produced when the thiocarbimide, dissolved in a small proportion of

benzene, was mixed with piperidine; heat was developed, and, after an interval, petroleum was added, the precipitated piperidyl derivative was then dissolved in dilute hydrochloric acid, filtered from a small quantity of dicamphorylthiocarbamide, and again precipitated with potassium hydroxide. Recrystallisation from alcohol gave well-formed, cubic prisms melting at  $188^{\circ}$ :

0.1047 gave 0.0853  $\text{BaSO}_4$ .  $S = 11.17$ .

$\text{C}_{16}\text{H}_{26}\text{ON}_2\text{S}$  requires  $S = 10.88$  per cent.

A solution containing 0.3130 gram in 25 c.c. of chloroform gave  $n_D^{20}$  1.4610 in a 2-dm. tube, whence  $[\alpha]_D^{20}$   $26.6^{\circ}$ . The substance is freely soluble in chloroform or pyridine, readily in benzene or acetone, and moderately in methyl alcohol or ethyl acetate, from which it crystallises in transparent prisms; boiling petroleum dissolves it sparingly, however, and it separates from this medium in lustrous, silky needles.

*Dicamphorylthiocarbamide*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{15}\text{O} \\ \text{CO} \end{smallmatrix}$ , is obtained by the action of water, acids, and alkalis on the thiocarbimide,

and crystallises from alcohol in colourless, glistening plates resembling thiocarbimide; it melts at  $176^{\circ}$ :

0.2050 gave 13.75 c.c. of nitrogen at  $16.5^{\circ}$  and 760 mm.  $N = 7.43$ .

0.1050 " 0.0639  $\text{BaSO}_4$ .  $S = 8.34$ .

$\text{C}_{11}\text{H}_{20}\text{O}_2\text{N}_2\text{S}$  requires  $N = 7.44$ ;  $S = 8.51$  per cent.

A solution containing 0.4832 gram in 25 c.c. of acetone gave  $n_D^{20}$  1.4610 in a 2-dm. tube, whence  $[\alpha]_D^{20}$   $54.3^{\circ}$ . The substance is readily soluble in chloroform, acetone, or glacial acetic acid, but only moderately in ether, ethyl acetate, methyl alcohol, or benzene; it is insoluble in cold petroleum, but dissolves very sparingly on boiling. When ethereal ferric chloride is added to a solution of the thiocarbimide in ether, no change is noticeable at first, but a pale brown, flocculent precipitate separates in the course of a few minutes.

Unlike thiocarbimide, dicamphorylthiocarbamide is insoluble in alkalis; it is also insoluble in dilute acids, and resists the action of concentrated hydrochloric acid. It appears to be capable of undergoing transformation into a pseudo-modification, because a solution of camphoryldithiocarbamic acid in excess of potassium hydroxide remains clear when heated at  $90^{\circ}$  during several hours, although camphorylthiocarbamide is insoluble in potassium hydrogen sulphide.

*Methyl camphorylthiocarbamate*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}\cdot\text{NH}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_3 \\ \text{CO} \end{smallmatrix}$ , is

formed when the mustard oil is heated in a sealed tube during five hours at about  $150^{\circ}$  with absolute methyl alcohol; it displays a tendency to form supersaturated solutions in methyl alcohol, but

may be conveniently recrystallised from petroleum, when it melts at  $118^{\circ}$ :

0.2268 gave 11.7 c.c. of nitrogen at  $17^{\circ}$  and 764 mm.  $N = 6.02$ .

$C_{12}H_{11}O_2NS$  requires  $N = 5.81$  per cent.

A solution containing 0.3645 gram in 25 c.c. of chloroform gave  $\alpha_D^{20} 1.10$  in a 2-cm. tube, whence  $[\alpha]_D^{20} 108.6^{\circ}$ . The substance is freely soluble in methyl and ethyl alcohols, chloroform, benzene, and ethyl acetate.

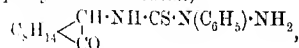
*The Camphorylphenylthiosemicarbazides.*

Camphorylthiocarbimide and phenylhydrazine interact very readily when brought together in moderately dilute solutions. A great number of experiments have been made with the object of determining the conditions favouring the production of each modification, but the two thiosemicarbazides appear to be formed simultaneously, and require to be separated by fractional crystallisation. The following two experiments are typical of many.

Eight grams of the thiocarbimide were dissolved in chloroform and treated with 5 grams of phenylhydrazine. When the solvent had evaporated spontaneously, the gummy residue was warmed with methyl alcohol, which caused crystals to separate on cooling; this product, weighing about 6 grams, was recrystallised from methyl alcohol, separating in thin, lustrous plates melting at  $183^{\circ}$ . The mother-liquors yielded a small proportion of the anhydride, melting at  $255^{\circ}$ , along with about 4 grams of needles, more freely soluble in methyl alcohol, and melting at  $163^{\circ}$ .

Nine grams of the thiocarbimide dissolved in 120 c.c. of ether, to which a small quantity of alcohol had been added, were cooled in ice, and treated with 6 grams of phenylhydrazine, also dissolved in ether: the liquid changed to a clear, tough jelly, which underwent but slight shrinkage during six hours. This was dissolved in 20—30 c.c. of hot alcohol and warmed until the ether was removed; 8 grams of the less fusible thiosemicarbazide were deposited from this solution, the mother-liquor yielding about 1 gram of the isomeride.

The camphorylphenylthiosemicarbazide,



which melts at  $183^{\circ}$ , is obtained with comparative ease, owing to its relatively sparing solubility, but it has the inconvenient property of yielding a tough, transparent jelly when dissolved in ether, alcohol, or petroleum, a peculiarity which has been recently noticed by E. Fischer and Abderhalden (*Ber.*, 1907, **40**, 3558) in connexion with a substance,  $C_{12}H_{12}O_2N_2$ , obtained from elastin by hydrolysis. We have made experiments to ascertain the minimum of material which

is capable of producing this jelly, and find that if the thiosemicarbazide is first dissolved in a small quantity of hot alcohol, and the solution diluted with petroleum, one part in 300 gives a tough, transparent jelly, which does not liquefy during twenty-four hours; after this period, however, the medium gradually becomes limpid, and the solid separates in well-defined crystals, which at first appear suspended in the jelly:

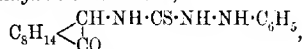
0.1886 gave 23.1 c.c. of nitrogen at 19° and 759 mm.  $N = 13.35$ .

0.1847 „ 0.1325  $\text{BaSO}_4$ .  $S = 9.85$ .

$\text{C}_{17}\text{H}_{23}\text{ON}_3\text{S}$  requires  $N = 13.25$ ;  $S = 10.09$  per cent.

A solution containing 0.3153 gram in 25 c.c. of chloroform gave  $[\alpha]_D^{25} 1.31$  in a 2-dm. tube, whence  $[\alpha]_D 59.5^\circ$ . The substance is insoluble in aqueous alkali, and is readily converted into the anhydride, described below, when the alcoholic solution is heated with a small quantity of hydrochloric acid, or when an attempt is made to re-crystallise the solid from glacial acetic acid. An estimation of the molecular weight in benzene gave an average of 338 units, the value calculated from the empirical formula  $\text{C}_{17}\text{H}_{23}\text{ON}_3\text{S}$  being 317.

The *camphorylphenylthiosemicarbazide*,



which melts at 163°, is produced in small quantities only, even under the most favourable conditions:

0.2270 gave 25.5 c.c. of nitrogen at 22° and 765 mm.  $N = 12.82$ .

0.1016 „ 0.0767  $\text{BaSO}_4$ .  $S = 10.36$ .

$\text{C}_{17}\text{H}_{23}\text{ON}_3\text{S}$  requires  $N = 13.25$ ;  $S = 10.09$  per cent.

A solution containing 0.2134 gram in 25 c.c. of chloroform gave  $[\alpha]_D^{25} 1.9$  in a 2-dm. tube, whence  $[\alpha]_D 58.5^\circ$ . Although the degree of optical activity is almost identical with that of the isomeric substance, the following colour tests serve to distinguish between the two materials; to render the comparison more convenient, the various reactions are tabulated alongside with those of the anhydride:

	M. p. 163°.	M. p. 183°.	Anhydride.
Concentrated sulphuric acid.	Rich blue.	Deep yellow.	Colourless.
Alcoholic copper acetate.	Intense bluish-green.	Intense, but transient, brown.	Transient brown, less intense.
Alcoholic copper nitrate.	Intense blue.	Blue, less intense.	Grass-green.
Alcoholic nickel acetate.	Colourless at first, purple on warming.	Grass-green.	No change.
Etheral ferric chloride.	No change.	Deep red.	No change.



	M. p. 163°.	M. p. 183°.	Anhydride.
Alcoholic silver nitrate.	White opalescence, pale brown on boiling.	White opalescence, pale black on boiling.	No change, even on boiling.
Ammoniacal silver nitrate.	Yellow coloration, becoming green; black precipitate on boiling.	White opalescence, intensifying to a brown precipitate on boiling.	Immediate yellow precipitate, which does not darken on boiling.
Boiling pyridine solution.	Deep orange coloration.	Pale yellow.	No change.

The anhydride,  $C_6H_5 \cdot \begin{matrix} CH \cdot NH \cdot CS \\ \diagup \quad \diagdown \\ N \quad N \end{matrix} \cdot C_6H_5$ , crystallises in small, lustrous needles melting at 235°:

0.2153 gave 26.8 c.c. of nitrogen at 20° and 762 mm.  $N = 14.28$ ,  
0.1007 " 0.0783  $BaSO_4$ .  $S = 10.68$ .

$C_{17}H_{15}N_3S$  requires  $N = 14.04$ ;  $S = 10.70$  per cent.

A solution containing 0.2823 gram in 25 c.c. of chloroform gave  $n_D^{20}$  1.412 in a 2-dm. tube, whence  $[a]_D^{20}$  274.5°. The substance is sparingly soluble in methyl and ethyl alcohols, ethyl acetate, or benzene, more readily, however, in acetone and chloroform; it is freely soluble in pyridine, but practically insoluble in petroleum.

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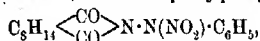
### CLXXXIII.—*Aromatic Amides and Imides of Camphoric Acid.*

By WILLIAM ORD WOOTTON.

THE derivatives of camphoric acid described in this communication were prepared with the object of obtaining an amino-compound, which, while displaying the stability and reactivity of an aromatic amine, should at the same time exhibit the optical properties usually associated with the presence of a camphor nucleus. It was thought that such a compound might prove useful in the study of certain racemic aldehydes, the resolution of which the author desires to effect.

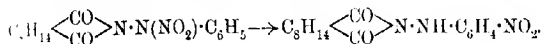
Since camphorylphenylhydrazide, an optically active and readily accessible substance, might be supposed to yield nitro-derivatives, and consequently aromatic amines, the action of nitric acid on this compound was first studied. It was found that the products of nitration were more complex than was at first supposed, the action of nitric

(sp. gr. 1.42) leading to the formation of a mixture of substances from which a new nitroamine, *N*-nitrocamphorylphenylhydrazide,



was isolated. It was incidentally discovered that the substance obtained by the action of nitrous acid on camphorylphenylhydrazide is *N*-nitrocamphorylphenylhydrazide, and not a nitro-compound as stated by E. M. Chaplin (*Ber.*, 1892, 25, 2565). Similar pairs of *N*-nitro- and *N*-nitroso-compounds have been obtained from two new amino-derivatives of camphorylphenylhydrazide.

The *N*-nitro-compounds appear to exhibit the property, characteristic of nitroamines in the aromatic series, of passing readily into isomeric nitro-compounds. Thus, when boiled with solvents or simply heated in fusion, the nitro-group migrates from the aminic group to one of the carbon atoms in the benzene nucleus :



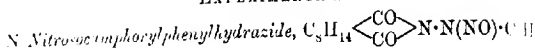
A mixture of isomeric *C*-nitro-compounds is probably produced, and it is intended to continue the study of this transformation.

The nitroso-derivatives in this series are very pale yellow, the corresponding *N*-nitro-derivatives are colourless, whilst the *C*-nitro-compounds have a yellow colour. The nitroso-compounds become colourless when cooled to the temperature of liquid air.

The complexity of this nitration has up to the present precluded the possibility of obtaining an aromatic amino-derivative of camphorylphenylhydrazide in a state of purity. It has been found, however, that, by condensing together camphoric anhydride and *p*-bromoaniline, in aniline is obtained; this, on nitration and subsequent reduction, yields a well-defined amino-compound which, in alcoholic solution, shows  $[\alpha]_D$  40.7°. The behaviour of this base towards aldehydes will be described in a further communication.

Attempts to prepare 4-amino- and 3-amino-phenyl- $\alpha$ -camphoramides through the condensation of camphoric anhydride with the *p*- and *m*-nitroanilines respectively were unsuccessful, owing to the difficulty with which these substances react. The 4-amino-compound was, however, ultimately obtained by the reduction of 4-benzeneazo-phenyl- $\alpha$ -camphoramidic acid,  $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_5$ , a substance which is interesting as being one of the few recorded instances of optically active aromatic azo-compounds.

## EXPERIMENTAL.



This substance is most conveniently prepared by treating camphorylphenylhydrazide dissolved in glacial acetic acid with the required quantity of sodium nitrite in 20 per cent. aqueous solution. The compound is precipitated by the addition of water and recrystallised in alcohol, from which it separates in yellow needles melting with decomposition at 157°. Repeated crystallisation from various solvents failed to remove the colour of the substance. A specimen prepared Chaplin's method was found to melt at 157°, and not to depress; melting point of the preceding preparation:

0.1179 gave 0.2722  $CO_2$  and 0.0663  $H_2O$ .  $C = 62.97$ ;  $H = 6.25$ .

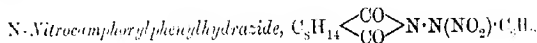
0.1014 " 0.2365  $CO_2$  and 0.0531  $H_2O$ .  $C = 63.69$ ;  $H = 5.82$ .

0.2318 " 27.6 c.c. nitrogen at 15° and 755 mm.  $N = 13.85$ .

$C_{16}H_{14}O_4N_2$  requires  $C = 63.79$ ;  $H = 6.31$ ;  $N = 13.95$  per cent.

0.4330 in 25 c.c. of chloroform in a 2-dm. tube gave  $a_D^{20} 0.42$ , whence  $[\alpha]_D^{20} 11.1^\circ$ .

This nitroso-compound gives the Liebermann reaction with intense colorations in all its phases. Reduction with aluminium amalgam in moist ethereal solution leads to the formation of camphorylphenylhydrazide and ammonia.



This was prepared by dissolving 10 grams of camphorylphenylhydrazide in 20 c.c. of glacial acetic acid and 10 c.c. of acetic anhydride. The solution was cooled in ice and treated with a mixture of 2 c.c. of nitric acid (sp. gr. 1.5) and 2 c.c. of acetic anhydride. After thirty minutes, the nitro compound was precipitated by the cautious addition of water. By recrystallisation from carbon disulphide or chloroform, in which the compound is very soluble, it was obtained in large, colourless prisms melting at 115—116° to a deep red liquid. The compound is soluble in alcohol or in glacial acetic acid, but if boiled with these solvents decomposition takes place:

0.0888 gave 0.1978  $CO_2$  and 0.0163  $H_2O$ .  $C = 60.75$ ;  $H = 5.89$ .

$C_{16}H_{14}O_4N_2$  requires  $C = 60.56$ ;  $H = 5.99$  per cent.

0.3591 in 20 c.c. of chloroform in a 2-dm. tube gave  $a_D^{20} 0.58$ , whence  $[\alpha]_D^{20} 16.1^\circ$ .

The fact that camphorylphenylhydrazide and ammonia are produced when this compound is reduced indicates that the nitro-group is attached to one of the carbon atoms in the benzene nucleus.

*N-Nitrosacamphoryl-4-bromophenylhydrazide*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$ .

This derivative was obtained, in the first instance, by treating camphorylphenylhydrazide (1 mol.) in glacial acetic acid solution with bromine (1 mol.). The product did not attain a constant melting point until it had been crystallised four times from glacial acetic acid and five times from alcohol, when it was obtained in colourless, lath-like crystals melting at 182–183°. It would appear that a small amount of an isomeride is produced in this bromination, probably *N-nitrosacamphorylphenylhydrazide* :

$d_{4}^{20} 1.202$  gave 17 c.c. of nitrogen at 20° and 762 mm.  $\text{N} = 7.83$ .

$d_{4}^{20} 1.68$ ,  $n_D^{20}$  0.1300 AgBr.  $\text{Br} = 22.42$ .

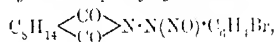
$\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2\text{Br}$  requires  $\text{N} = 7.98$  ;  $\text{Br} = 22.79$  per cent.

$d_{4}^{20} 1.64$  in 20 c.c. of absolute alcohol in a 2-dem. tube gave  $a_D$  0.66°,  $[\alpha]_D^{20}$  26.9°.

When boiled for some hours with 10 per cent. aqueous potassium hydroxide, potassium camphorate, phenol, bromobenzene, and ammonia were produced.

The orientation of the bromine atom was accomplished by combining camphoric anhydride with *p*-bromophenylhydrazine. When these were heated together in molecular proportions at 130–150°, a brown action ensued. The brown, glassy mass obtained on cooling was recrystallised from alcohol, when colourless needles, melting at 182–183°, were obtained which were identical with the product of the foregoing bromination, inasmuch as they did not depress the melting point of the first preparation.

*N-Nitrosacamphoryl-4-bromophenylhydrazide*,



was obtained as a crystalline precipitate when sodium nitrite in aqueous solution was added to a glacial acetic acid solution of camphoryl-*p*-bromophenylhydrazide. When recrystallised successively from alcohol and carbon disulphide, it formed fine, pale yellow needles melting without decomposition at 154–155° :

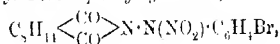
$d_{4}^{20} 1.35$  gave 0.2100  $\text{CO}_2$  and 0.0506  $\text{H}_2\text{O}$ .  $\text{C} = 50.46$  ;  $\text{H} = 4.95$ .

$d_{4}^{20} 1.710$ ,  $n_D^{20}$  20.7 c.c. of nitrogen at 16° and 756 mm.  $\text{N} = 11.36$ .

$\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2\text{Br}$  requires  $\text{C} = 50.53$  ;  $\text{H} = 4.71$  ;  $\text{N} = 11.05$  per cent.

$d_{4}^{20} 1.68$  in 20 c.c. of chloroform in a 2-dem. tube gave  $a_D$  0.70°,  $[\alpha]_D^{20}$  18.1°.

*N-Nitrosacamphoryl-4-bromophenylhydrazide*,



Yield, 0.41.

G K

was formed when a mixture of acetic anhydride and nitric acid (sp. gr. 1.5), was slowly added to a solution of camphoryl-4-benzophenylhydrazide in glacial acetic acid. The white, crystalline precipitate was washed successively with glacial acetic acid, acetone, and ether; it was thus obtained in the pure state and quite colorless. It is only sparingly soluble in the usual organic solvents:

0.1669 gave 0.1923  $\text{CO}_2$  and 0.0462  $\text{H}_2\text{O}$ .  $\text{C} = 49.05$ ;  $\text{H} = 4.88$ .

0.2253 " " 21.0 c.c. of nitrogen at 16° and 755 mm.  $\text{N} = 19.65$ .

$\text{C}_{20}\text{H}_{14}\text{O}_4\text{N}_2\text{Br}$  requires  $\text{C} = 48.48$ ;  $\text{H} = 4.55$ ;  $\text{N} = 10.60$  per cent.

0.3432 in 20 c.c. of chloroform in a 2-cm. tube gave  $n_D^{20} 1.497$ , whence  $\mu_D 1.490$ .

When slowly heated, this compound becomes yellow at about 140°, and on further heating melts very indefinitely. If, however, a capillary containing it is placed in a bath at 155°, it melts sharply to a dark red liquid at 159–160°. The original compound is only sparingly soluble in alcoholic potash, giving a colorless solution; after fusion, however, the product is freely soluble in this reagent, the solution being blood-red at first, but becoming purple when diluted with water and allowed to remain for some time. When the *N*-nitro-compound is boiled for a few minutes in glacial acetic acid, it passes into solution, the liquid gradually becoming yellow. The addition of water occasions the formation of a yellow precipitate, from which, however, no definite crystallisable substance has yet been isolated. Like the product of fusion, this precipitate is readily soluble in alcoholic potash to a deep red solution; unlike the original *N*-nitro-compound, it is freely soluble in the usual organic solvent. These facts are explicable on the supposition that, under the action of heat the nitro-group has wandered from the amino-group to the benzene nucleus, where its proximity to the aminic hydroxyl group has conferred sufficient acidity on the compound to enable it to form soluble salts when treated with potassium or sodium hydroxide. This is confirmed by the behaviour of the yellow substance on reduction, when an almost colourless basic product is obtained. This can be diazotised; the diazo-solution gives a red coloration when added to alkaline  $\beta$ -naphthol, thus indicating the formation of an amino-compound.

The *N*-nitro-derivative on reduction yields camphoryl-4-benzophenylhydrazide and ammonia.

*Camphoryl-4-benzophenylhydrazide*,  $\text{C}_8\text{H}_{14}\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ .

Camphorylphenylhydrazide (1 mol.) was dissolved in glacial acetic acid and treated with bromine (2 mols.). After twelve hours the greater part of the dibromo-derivative had separated in glacial

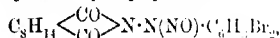
When recrystallised from glacial acetic acid, it melted at 129°:

0.229 gave 18.1 c.c. of nitrogen at 17° and 765 mm.  $N = 6.47$ .

0.2549 „ 0.2299 AgBr.  $Br = 36.93$ .

$C_{16}H_{11}O_2N_2Br_2$  requires  $N = 6.51$ ;  $Br = 37.21$  per cent.

*N Nitrocamphoryldibromophenylhydrazide*,



Prepared from hot alcohol in small, heavy, pale yellow, rhombic crystals melting at 147–148°:

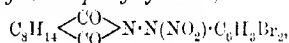
0.202 gave 19.8 c.c. of nitrogen at 15° and 755 mm.  $N = 9.20$ .

0.2287 „ 0.1870 AgBr.  $Br = 34.73$ .

$C_{16}H_{17}O_3N_3Br_2$  requires  $N = 9.15$ ;  $Br = 34.85$  per cent.

0.2776 in 15 c.c. of chloroform in a 2-dcm. tube gave  $n_D^{20} 1.070$ ,  $d_4^{20} 1.090$ ,  $[\alpha]_D^{19} 19.0^\circ$ .

*N Nitrocamphoryldibromophenylhydrazide*,



Prepared in a similar manner to the corresponding monobromo-derivative, crystallised from a mixture of acetone and alcohol in glistening, colourless, rhombic prisms melting at 140–142° with decomposition:

0.2333 gave 0.1834 AgBr.  $Br = 33.46$ .

$C_{16}H_{17}O_3N_3Br_2$  requires  $Br = 33.68$  per cent.

0.2412 in 15 c.c. of chloroform in a 2-dcm. tube gave  $n_D^{20} 1.046$ ,  $d_4^{20} 1.099$ ,  $[\alpha]_D^{19} 10.9^\circ$ .

#### *Derivatives of $\alpha$ -Camphoramic Acid.*

*p-Bromophenyl- $\alpha$ -camphoramic acid*,  $(CO_2H \cdot C_8H_{11} \cdot CO) \cdot NH \cdot C_6H_4Br$ .

When camphoric anhydride and *p*-bromoniline are heated together in molecular proportions at 120°, combination takes place with considerable evolution of heat. The molten material rapidly sets to a brittle, crystalline mass, which, when crystallised two or three times from alcohol, forms thin, brilliant prisms melting at 206–207°.

0.551 gave 0.0811 AgBr.  $Br = 22.51$ .

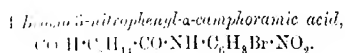
$C_{16}H_{20}O_3NBr$  requires  $Br = 22.60$  per cent.

0.612 in 25 c.c. of absolute alcohol in a 2-dcm. tube gave  $n_D^{20} 1.260$ ,  $d_4^{20} 1.170$ ,  $[\alpha]_D^{19} 47.0^\circ$ .

This acid is freely soluble in acetone or alcohol, sparingly so in ether, and insoluble in water or light petroleum. It is readily soluble in aqueous solutions of alkalis or alkali carbonates.

The *acid* (I) was obtained as a bulky, gelatinous mass, possessing a strongly viscous taste.

The *acid* (I) is sparingly soluble in hot water, from which, on cooling, separates in minute leaflets.



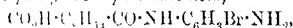
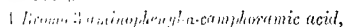
To a mixture of 30 c.c. of nitric acid (sp. gr. 1.5) and 24 c.c. of acetic acid are added, in small portions at a time, 10 grams of bromophenyl camphoronic acid. After thirty minutes, the mixture is poured on to ice, when the nitro-compound separates as a yellow precipitate. After recrystallisation from alcohol, in which it is only moderately soluble, it is obtained in bright yellow, hexagonal plates melting at 201–206°.

0.1900 gave 0.0660 AgBr. Br = 20.16.

$\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}_2\text{Br}$  requires Br = 20.05 per cent.

0.2066 in 20 c.c. of absolute alcohol in a 2-dem. tube gave  $n_D^{20}$  = 1.47 whence  $n_D^{25}$  = 1.481.

The *acid* salt of this acid forms yellow leaflets readily soluble in water. When boiled with sodium hydroxide, it is hydrolysed with formation of sodium camphorate and 4-bromo-3-nitroaniline. The latter substance after recrystallisation was found to melt at 112 (Höber gives 111°).



is most conveniently prepared by dissolving 1 part of the foregoing nitro-acid in excess of aqueous ammonia and adding 4 parts of ferrous sulphate dissolved in water in small portions at a time. When the ferrous hydroxide at first precipitated has completely changed into ferric hydroxide, the mixture is heated on the water-bath for a short time with frequent stirring and then filtered by the aid of the pump. On neutralising the filtrate with acetic acid, the amino-compound separates as a bulky, white precipitate. The yield approximates 75 per cent. of the theoretical. By recrystallisation from dilute alcohol, the substance is obtained in stellate clusters of colourless needles melting at 207–208°.

0.2194 gave 11.4 c.c. of nitrogen at 20° and 758 mm. N = 7.43.

0.2824 „ 0.1414 AgBr. Br = 21.31.

$\text{C}_{17}\text{H}_{15}\text{O}_5\text{N}_2\text{Br}$  requires N = 7.59; Br = 21.68 per cent.

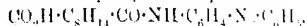
0.1878 in 25 c.c. of absolute alcohol in a 2-dem. tube gave  $n_D^{20}$  = 1.50 whence  $n_D^{25}$  = 1.497.

This amino-acid is readily soluble in aqueous alkalis and alkali carbonates, but less so in concentrated hydrochloric acid. It

*Acetyl derivative* is obtained as a white, amorphous precipitate by passing acetyl chloride into a solution of the base in acetone. When subjected to the action of nitrous acid, the hydrochloride appears to form a colorless, insoluble diazo-anhydride.

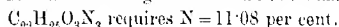
The *acetyl* derivative is freely soluble in aqueous alkalis, and separates from dilute alcohol in iridescent leaflets melting at 217–218°.

*4-Benzeneazophenyl- $\alpha$ -camphoric acid.*



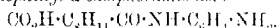
This compound results when equimolecular weights of camphoric anhydride and aminoazobenzene are heated together for a short time at 260–280°. It is separated from unchanged material by extraction with aqueous ammonia, reprecipitated from the ammoniacal solution by addition of acid, and crystallised several times from alcohol. The compound is thus obtained in beautiful orange-red needles melting at 223–224°.

0.2030 gave 20.0 c.c. of nitrogen at 23° and 760 mm.  $\text{N} = 11.10$ .



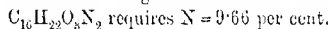
0.1483 in 25 c.c. of absolute alcohol in a 2-cm. tube gave  $\alpha_D^{20} 1.04$ ,  $[\alpha]_D^{20} 87.7^\circ$ .

This compound dissolves in concentrated sulphuric acid to a deep yellow solution. The alkali salts are yellow and soluble in water. The *calcium* salt, however, is excessively insoluble; it is precipitated from the yellow needles when a few drops of hard water are added to a solution of one of the alkali salts. Reduction of an alcoholic solution of the acid by means of stannous chloride results in the formation of 4-aminophenyl- $\alpha$ -camphoric acid.



This somewhat unstable substance was obtained as a white or light grey amorphous powder, readily soluble in alcohol, acetone, or chloroform, and in solutions of sodium hydroxide or sodium carbonate, but insoluble in water or light petroleum. From solutions, however, it separated in a resinous condition, and became solid only when left for several days; it could not be obtained crystalline.

0.2202 gave 20.4 c.c. of nitrogen at 23° and 752 mm.  $\text{N} = 9.92$ .



On attempting to acetylate this base, it underwent decomposition. The *acetyl* derivative, however, was ultimately obtained by heating either camphoric anhydride and 4-aminoacetanilide either alone or with a solvent. From dilute acetic acid, the compound crystallises in shining leaflets melting at 233–254°. An attempt to prepare the



being made by the fractional hydrolysis of this acetyl derivative, was successful, only *p*-phenylenediamine and its oxidation product being obtained.

*Derivatives of N-Phenylcamphorimide.*

The 1-*trans* derivative,  $C_8H_{11}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}N \cdot C_6H_4Br$ , is produced when *p*-phenylcamphoramic acid is heated for an hour with glacial acetic acid and acetic anhydride. Unchanged bromo-acid is recovered on reaction with aqueous ammonia. The new imide forms pale yellow crystals, soluble in hot alcohol and melting at  $180-181^\circ$ :

0.192 g. gave 0.1074 AgBr. Br = 23.57.

$C_8H_{11}O_2NBr$  requires Br = 23.80 per cent.

The 1-*trans*-3-*nitro* derivative,  $C_8H_{11}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}N \cdot C_6H_3Br \cdot NO_2$ , is easily prepared in quantitative yield when the preceding compound is dissolved in cold nitric acid (sp. gr. 1.5). From hot alcohol crystalline in clusters of short, pale yellow needles which melt at  $171-172^\circ$ . When treated with tin and hydrochloric acid in alcohol, reduction to the corresponding amino-compound is effected.

0.1337 gave 8.7 c.c. of nitrogen at  $19^\circ$  and 754 mm. N = 7.46.

$C_8H_{11}O_2N_2Br$  requires N = 7.35 per cent.

The 1-*trans*-3-*amino* derivative,  $C_8H_{11}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}N \cdot C_6H_3Br \cdot NH_2$ , somewhat ill-defined base, dissolving freely in alcohol, acetone, chloroform, is deposited on cooling the warm solutions as a colorless oil which on trituration is converted into a white, microcrystalline solid melting at about  $130^\circ$ :

0.1257 g. gave 8.6 c.c. of nitrogen at  $25^\circ$  and 762 mm. N = 7.66.

$C_8H_{11}O_2N_2Br$  requires N = 7.98 per cent.

A solution of this base in acetone is feebly dextrorotatory.

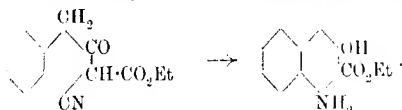
The *trans*-*trans*-biphenyl is decomposed by water; on diazotisation, it forms a clear solution which, when added to alkaline  $\beta$ -naphthol, yields a scarlet azo compound.

R. VAN DER LIND, of STENEC,  
SOUTH KENSINGTON, S.W.

CLXXXIV — *Ethyl  $\alpha$ -Cyano- $\gamma$ -phenylacetoacetate.*

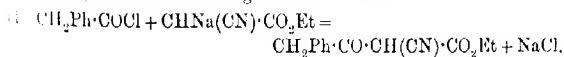
By ARTHUR RICHARD SMITH and JOCELYN FIELD THORPE.

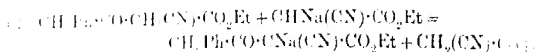
When it had been proved that ethyl  $\beta$ -imino- $\alpha$ -cyano- $\gamma$ -phenylbutyrate on treatment with concentrated sulphuric acid into ethyl 2-naphthylenediamine-2-carboxylate (Trans., 1906, 89, 1906), it was of importance to ascertain the nature of the reaction which takes place between the corresponding ketone, namely, ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate, and concentrated sulphuric acid, since it might be expected that in this case ring formation would also take place in the production of ethyl 4-amino-2-naphthol-3-carboxylate, thus :



It was found, however, that although concentrated sulphuric acid instantly acted on the ketone, forming a deep malachite-green solution, the products formed appeared to be of high molecular complexity, and no crystalline compound has as yet been isolated from the reaction. There is, however, a great resemblance between these products and those which are formed to so large an extent when ethyl  $\beta$ -imino- $\alpha$ -cyano- $\gamma$ -*p*-tolylbutyrate and ethyl  $\beta$ -imino- $\alpha$ -cyano- $\gamma$ -*p*-tolylbutyrate are treated with concentrated sulphuric acid (Trans., 1907, 91, 1687), and it is hoped that the identification of these will lead to a solution of the above reaction. In the meantime, since during the course of the investigation a considerable quantity of ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate has been prepared, we give in the present paper an account of its properties and those of some of its derivatives, since the published data concerning them have been in some instances incorrectly recorded.

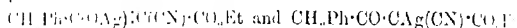
Ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate was originally prepared by Lieber (Ber., 1888, 21, 644) by the action of phenylacetyl chloride on the sodium compound of ethyl cyanoacetate, and was described as a yellow oil not capable of being distilled under diminished pressure without undergoing decomposition. We have prepared large quantities of this ethyl salt in a crystalline condition by employing the following modification of Haller's process. Two molecular proportions of the sodium compound were condensed with one molecular equivalent of the acid chloride, when the following reactions ensued :





The product therefore consisted of the sodium compound of *α*-cyano-*γ*-phenylacetoacetate and ethyl cyanoacetate. Since the former derivative is quite stable in aqueous solution, it dissolved in boiling water, and on extracting with ether the whole of the ethyl cyanoacetate was removed, leaving an aqueous solution from which, on acidifying, ethyl *α*-cyano-*γ*-phenylacetoacetate was precipitated as a colourless oil. The ethyl salt prepared in this way was not readily oxidised without decomposition, yielding a colourless distillate and a solid on cooling.

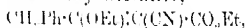
The salts of ethyl *α*-cyano-*γ*-phenylacetoacetate are remarkable chloride substances, and the ammonium salt can be recrystallised from water without change. The action of alkyl iodides on the silver salt gives results of some interest, since the salt reacts as an atropine mixture of the two forms:



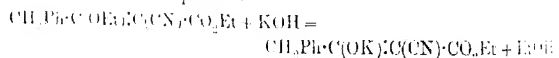
Thus, when the silver salt is treated in dry ether with ethyl iodide, an ethyl derivative can be prepared which, although distilling at constant temperature, is nevertheless a mixture of the two components.

$\text{CH}_2\text{Ph}\cdot\text{C}(\text{OEt})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$  and  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CEt}(\text{CN})\cdot\text{CO}_2\text{Et}$  is a fact which is proved in the following way. The oil showed no tendency to crystallise even when kept for several weeks in the ice-chamber, but ultimately, during an experiment on the action of bromine in carbon tetrachloride solution on the oil, crystals were obtained which were added to the oil immediately started crystallisation. After the lapse of a month, when the growth of the crystals appeared to have ceased, they were separated from the supernatant oil by means of petroleum, recrystallised, and obtained in well-defined crystals melting sharply at 66°.

These crystals are the ethoxy-derivative,



a fact which is clearly proved by their behaviour on warming with dilute aqueous potassium hydroxide, when hydrolysis ensues in accordance with the equation:



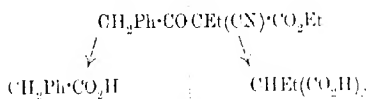
yielding a potassium compound which on acidifying is transformed into ethyl *α*-cyano-*γ*-phenylacetoacetate. On prolonged boiling with aqueous alkali, the hydrolysis of course proceeds further, and the potassium salts of phenylacetic and malonic acids are the end products.

Moreover, the ethoxy-derivative does not combine with phos-

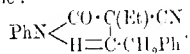
to form a pyrazolone, a reaction which is readily effected with ethyl  $\alpha$ -cyano- $\gamma$ -phenyl  $\alpha$ -ethylacetoacetate, but it yields a well-defined anilide melting at 85°.

The oil which had been separated from the crystals by the aid of porous porcelain was extracted and isolated. It boiled constantly at 191° (20 mm.), but could not be induced to crystallise; moreover, the addition of a crystal of the ethoxy-derivative failed to induce crystallisation. It is evident that this liquid is the ethyl derivative of the formula  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , for the following reasons:

On alkaline hydrolysis, the ethyl salt is converted into phenyl malonic acid and ethylmalonic acid in accordance with the scheme:



On treatment with phenylhydrazine, it yields 4 cyano-1-phenyl 3-phenyl-2-ethylpyrazolone:



On treatment with aniline, it yields an anilide melting at 129°, quite different from that derived from the isomeric ethoxy-derivative. Under the experimental conditions described, the *O*-ethyl derivative is obtained to a much greater extent than the *C*-ethyl compound, the proportion being about 4:1. We could not, however, be quite certain if the *C*-ethyl compound was entirely free from the *O*-derivative. This is therefore another instance of "anomalous replacement" (compare Lander, *Trans.*, 1903, **83**, 415), of which there are now so many, especially among the nitrogen compounds.

Many experiments were tried with the object of converting ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate into the corresponding amino-derivative, but without success. The ammonium salt, which crystallised well from water, probably has the formula  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{ONH}_4)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , and it was hoped that by eliminating water from this salt an amino-derivative of the formula  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$  would be obtained which would either be identical or isomeric with ethyl  $\beta$ -imino- $\gamma$ -phenylbutyrate,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , which had been previously prepared by the interaction of phenylacetonitrile and the sodium compound of ethyl cyanoacetate (*Trans.*, 1906, **89**, 1916). The ammonium salt, however, evolved ammonia on being heated at 100°, being transformed into the ethyl salt from which it was derived; and on being treated with anhydride and other dehydrating agents brought about a similar

result, and when the salt was rapidly distilled it was partly decomposed into phenylacetamide and partly into a substance which probably the anhydride of  $\alpha$ -cyano- $\gamma$ -phenylacetoacetic acid. The cause of this decomposition is most likely due to the fact that it is impossible to eliminate from the ammonium salt the one molecule of water of crystallization with which it is always accompanied.

*Preparation of Ethyl  $\alpha$ -Cyano- $\gamma$ -phenylacetoacetate,*  
 $C_9H_9N_2O_4 \cdot CO \cdot CH(CN) \cdot CO_2Et$ .

In order to obtain this substance, the dried sodium compound of  $\alpha$ -cyanoacetate was first prepared by adding the ethyl salt to a solution containing the requisite quantity of sodium dissolved in ethyl alcohol, then adding an equal volume of dry ether, filtering, washing thoroughly with dry ether, and, finally, drying in an evacuated desiccator over sulphuric acid. Two molecular proportions of the dry salt were then taken, suspended in dry ether, and cautiously mixed in a flask fitted with a water condenser with one molecular proportion of phenylacetyl chloride. The reaction started at once, and was practically at an end shortly after the last portion of phenylacetyl chloride had been added, although, in order to make certain that the condensation had finished, an hour was allowed to elapse before the product was worked up.

Water was then added, the mixture well shaken, and the ethereal liquid separated. The product, which consisted of a mixture of ethyl  $\alpha$ -cyanoacetate and the sodium compound of ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate, formed in accordance with the equations given on pp. 1899 and 1900, was therefore separated by the above process, the ethyl cyanacetate remaining dissolved in the ether and the sodium compound of the condensation product remaining in solution in the aqueous extract, which was extracted once with ether and then made acid with hydrochloric acid. The heavy oil which then separated was extracted with ether, the ethereal solution dried, and evaporated, when a residue was left which still filled constantly at  $178^\circ$  (20 mm.) as a colourless solid which became solid on cooling. The solid was spread on a glass plate to remove oily impurities and then crystallised from ethyl alcohol, separating from the well-cooled solution in large, colourless prisms melting at  $24^\circ$ .

0.4582 gave 0.3894  $CO_2$  and 0.0826  $H_2O$ .  $C = 67.17$ ;  $H = 5.59$ .  
 $C_{12}H_{11}O_4N$  requires  $C = 67.5$ ;  $H = 5.6$  per cent.

Ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate in alcoholic solution gives a deep red colour with ferric chloride. It is a strong acid and readily decomposes alkaline carbonates. The sodium and potassium salts, prepared either by the action of the carbonates or by the action of the bar-

are precipitated from their solutions by excess of the reagent, and they are oily substances difficult to obtain pure.

The *ammonium* salt,  $C_{13}H_{15}O_3N_3 \cdot H_2O$ , is best prepared in quantity by dissolving 20 grams of the ethyl salt in 150 c.c. of water heated to  $50^\circ$ , adding excess of ammonia, and allowing the clear solution to stand, when colourless crystals of the salt slowly separate. If crystallised from warm water in slender needles without undergoing appreciable dissociation, although, when boiled, the solution slowly loses ammonia and becomes cloudy owing to the separation of ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate :

0.285 gave 27.8 c.c. of nitrogen at  $21^\circ$  and 767 mm.  $N = 10.71$ .

$C_{13}H_{15}O_3N_3$  requires  $N = 10.5$  per cent.

It was not found possible to eliminate the water of crystallisation from the ammonium salt, since, when heated at  $100^\circ$  or when treated by dehydrating agents, it gradually lost ammonia, being reconverted to the ethyl salt from which it was derived.

The *silver* salt,  $C_{13}H_{12}O_3NAg$ , was obtained as a white precipitate by adding a solution of silver nitrate to an aqueous solution of the ammonium salt :

0.2586 gave 0.0824 Ag.  $Ag = 31.86$ .

$C_{13}H_{12}O_3NAg$  requires  $Ag = 31.95$  per cent.

The *aniline- $\gamma$ -phenylacetacetanilide*,  $CH_2Ph \cdot CO \cdot CH(CN) \cdot CO \cdot NHPh$ , can be prepared by boiling ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate with excess of aniline for a few minutes and pouring the product into excess of dilute hydrochloric acid. The oil which remains undissolved slowly crystallises, and can be purified by recrystallisation from alcohol, from which solvent it separates in long, colourless needles melting at  $145^\circ$  :

0.770 gave 0.4769  $CO_2$  and 0.0843  $H_2O$ .  $C = 73.48$ ;  $H = 5.23$ .

$C_{17}H_{14}O_2N_2$  requires  $C = 73.4$ ;  $H = 5.0$  per cent.

The anilide gives a deep red colour in alcoholic solution with ferric chloride, and is soluble in aqueous solutions of caustic alkalis. On treatment with dilute sulphuric acid, it is completely decomposed into malonic acid, and phenylacetic acid.

The *ortho-1-phenyl-3-benzylpyrazolon*,  $PhN \begin{smallmatrix} \diagup CO \cdot CH \cdot CN \\ \diagdown N = C \cdot CH_2Ph \end{smallmatrix}$ , is prepared by the action of phenylhydrazine on ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate. The ethyl salt is dissolved in glacial acetic acid and, after being mixed with a solution of phenylhydrazine in acetic acid, is boiled for a few minutes. On cooling, a copious, crystalline precipitate separates, which can be crystallised from absolute alcohol, when it is obtained in slender, colourless plates melting at  $173^\circ$  :

0.255 gave 30.8 c.c. of nitrogen at 29° and 754 mm.  $N = 15.7$ ;

$C_9H_9O_2N$  requires  $N = 15.2$  per cent.

*Effect of Heat on the Ammonium Salt of Ethyl  $\alpha$ -Cyano- $\gamma$ -phenylacetacetate.*

As already mentioned, the above ammonium salt crystallises with one molecule of water of crystallisation, from which it cannot be separated at the same time undergoing decomposition. Numerous experiments were tried with the object of causing the compound to give up water and pass into the corresponding amino-derivative, and which was the action of heat under different conditions. When ammonium salt is heated at 100° under ordinary pressure, ammonium chloride and ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetacetate is formed. When, however, it is rapidly heated under 20 mm. pressure, a rapid decomposition takes place leading to the formation of phenylacetamide, and another substance which seems to be the amide of  $\alpha$ -cyano- $\gamma$ -phenylacetoacetic acid. The ammonium salt which had been placed for several days in an evacuated desiccator over sulphuric acid, heated at 150° under a pressure of 29 mm. in an inverted distilling flask until the evolution of gas had ceased; when the residue, which solidified on cooling, was freed from oil by spreading on a porcelain plate. The white, crystalline solid was then treated with dilute sodium carbonate solution and filtered, the insoluble matter being crystallised from water, from which it separated in lustrous plates melting at 155°:

0.4747 gave 0.4543  $CO_2$  and 0.1079  $H_2O$ .  $C = 70.92$ ;  $H = 6.75$ ;

$C_9H_9ON$  requires  $C = 71.1$ ;  $H = 6.7$  per cent.

The compound gave phenylacetic acid on hydrolysis with aqueous potassium hydroxide, and was therefore phenylacetamide.

The sodium carbonate solution from the above substance yielded a crystalline precipitate on acidifying, which was collected and recrystallised from alcohol, when it was obtained in lustrous laminae melting at 167°:

0.4774 gave 0.4421  $CO_2$  and 0.0801  $H_2O$ .  $C = 65.19$ ;  $H = 5.16$ ;

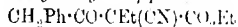
0.4688 gave 18.3 c.c. of nitrogen at 15° and 770 mm.  $N = 13.24$ ;

$C_9H_7O_2N_2$  requires  $C = 65.3$ ;  $H = 4.9$ ;  $N = 13.8$  per cent.

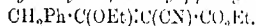
The compound gives a deep red coloration with ferric chloride, is slowly hydrolysed on prolonged boiling with aqueous potassium hydroxide, yielding phenylacetic acid and malonic acid, but its hydrolysis takes place with great difficulty, much more so than we have been expected in the case of an amide, and it is therefore possible that this compound may have a constitution other than that assigned to it by us.

action of dehydrating agents was also tried in order to eliminate the ammonium salt, but without avail. Thus, for example, heating with acetic anhydride completely transformed the salt into sodium acetate and ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate, the action of other dehydrating agents producing a similar result.

*Preparation of Ethyl  $\alpha$ -Cyano- $\gamma$ -phenyl  $\alpha$ -ethylacetoacetate,*



*and Ethyl  $\alpha$ -Cyano- $\beta$ -ethoxy- $\gamma$ -phenylcrotonate,*



The sodium compound of ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate does not react with alkyl iodides, and in order to prepare the ethyl derivative it was necessary to prepare the silver compound of the ethyl salt and then to treat it, suspended in ether, with the alkyl iodide. The well known silver compound, prepared in the manner already described on page 186, was suspended in dry ether in a flask fitted with a reflux condenser, after being mixed with excess of ethyl iodide, heated on a water bath until a test portion indicated that all the silver compound had been converted into silver iodide. The product was then filtered and the filtrate evaporated free from ether, when an oily substance remained which distilled constantly at  $191^\circ$  (20 mm.). The following analysis proved that this compound possessed the formula  $\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}$ :

0.178 g. gave 0.5015  $\text{CO}_2$  and 0.1205  $\text{H}_2\text{O}$ .  $\text{C} = 69.21$ ;  $\text{H} = 6.77$ .

$\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C} = 69.5$ ;  $\text{H} = 6.5$  per cent.

*Ethyl  $\alpha$ -Cyano- $\beta$ -ethoxy- $\gamma$ -phenylcrotonate.*—The oil described above showed no signs of crystallising even when cooled to a low temperature, and it was therefore concluded that the compound was a liquid. Nevertheless, an experiment was tried with the object of ascertaining the action of bromine in chloroform solution on the ethyl salt. It was found that only a trace of the halogen was absorbed, but on evaporating the product free from chloroform a residue was obtained which rapidly solidified, and a crystal added to the liquid ethyl compound caused it to crystallise slowly. It was left for a month in the dark, when, since the growth of the crystals appeared to have ceased, it was spread on porous porcelain to remove the considerable quantity of oil which had not solidified and then recrystallised from petroleum (b. p.  $80^\circ$ – $90^\circ$ ) containing a little benzene, being obtained in large, colourless prisms melting at  $66^\circ$ :

0.1583 g. gave 0.4042  $\text{CO}_2$  and 0.0953  $\text{H}_2\text{O}$ .  $\text{C} = 69.63$ ;  $\text{H} = 6.68$ .

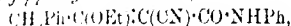
$\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}$  requires  $\text{C} = 69.5$ ;  $\text{H} = 6.5$  per cent.

The ethyl salt is quite insoluble in alkaline carbonates and in cold



acetic alkalis. It gives no coloration in alcoholic solution with ferric chloride.

*ethyl  $\alpha$ -cyano- $\beta$ -ethoxy- $\gamma$ -phenylcrotonamide,*



was prepared by boiling the above ethyl salt with excess of ammonia for ten minutes and pouring the product into dilute hydrochloric acid.

The oil which remained undissolved quickly solidified, and was purified by recrystallisation from alcohol, from which solvent it separated in colourless, rhombic prisms melting at  $85^\circ$ :

0.2148 gave 17.0 c.c. of nitrogen at  $19^\circ$  and 768 mm.  $N=9.1\%$ .

$\text{C}_{15}\text{H}_{17}\text{O}_2\text{N}_2$  requires  $N=9.1$  per cent.

When ethyl  $\alpha$ -cyano- $\beta$ -ethoxy- $\gamma$ -phenylcrotonate is warmed with dilute aqueous potassium hydroxide, it rapidly passes into solution, and on acidifying the product immediately after complete solution, a white crystalline oil is precipitated which on extraction with ether furnished ethyl  $\alpha$ -cyano- $\gamma$ -phenylacetoacetate melting at  $26^\circ$ :

0.1956 gave 0.1177  $\text{CO}_2$  and 0.0873  $\text{H}_2\text{O}$ .  $C=67.60$ ;  $H=5.77$ .

$\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$  requires  $C=67.5$ ;  $H=5.6$  per cent.

The compound was further identified by its conversion into an amide melting at  $115^\circ$ .

If the heating is continued after all the ethyl salt has dissolved in the aqueous potassium hydroxide, ammonia is evolved, and the final product consists of phenylacetic acid and malonic acid.

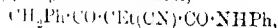
*Ethyl  $\alpha$ -Cyano- $\alpha$ -ethyl- $\gamma$ -phenylacetoacetate.*—The porous porcelain which had been used to dry the crystals described above, was broken into small pieces and extracted in a Soxhlet apparatus by means of ether. The ethereal solution on evaporation yielded an oil which distilled at  $190-191^\circ$  (20 mm.) as a viscid, colourless liquid:

0.1977 gave 0.5041  $\text{CO}_2$  and 0.1187  $\text{H}_2\text{O}$ .  $C=69.54$ ;  $H=6.67$ .

$\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$  requires  $C=69.5$ ;  $H=6.6$  per cent.

The compound, which was quite insoluble in dilute aqueous potassium hydroxide even on warming, could not be induced to dissolve even in a freezing mixture. It gave no coloration with ferric chloride.

*ethyl  $\alpha$ -cyano- $\alpha$ -ethyl- $\gamma$ -phenylacetoacetamide,*



was prepared by boiling a solution of the ethyl salt in ammonia for a few minutes and pouring the product into excess of dilute hydrochloric acid. The crystalline substance which remained undissolved was filtered and purified by recrystallisation from alcohol, when it was obtained in colourless needles melting at  $129^\circ$ :

0.2078 gave 19.6 c.c. of nitrogen at  $20^\circ$  and 769 mm.  $N=9.2\%$ .

$\text{C}_{19}\text{H}_{19}\text{O}_2\text{N}_2$  requires  $N=9.1$  per cent.

*Ethyl-1-phenyl-3-benzylethylpyrazolone*,  $\text{PhN} \begin{smallmatrix} \text{CO} \cdot \text{C}_6\text{H}_5 \cdot \text{CN} \\ \text{N} = \text{C} \cdot \text{CH}_2 \cdot \text{Ph} \end{smallmatrix}$ , was prepared by heating a solution of the ethyl salt in acetic acid with a solution of phenylhydrazine acetate. On cooling, crystals slowly appeared, which when purified by recrystallisation from alcohol formed colourless needles melting at  $167^\circ$  :

0.219 gave 27.1 c.c. of nitrogen at  $19^\circ$  and 757 mm.  $\text{N} = 14.00$ .

$\text{C}_{19}\text{H}_{17}\text{ON}_3$  requires  $\text{N} = 13.9$  per cent.

*Hydrolysis of Ethyl  $\alpha$ -Cyano- $\alpha$ -ethyl- $\gamma$ -phenylacetate to Phenylacetic and Ethylmalonic Acids.*

The hydrolysis was effected by dissolving the ethyl salt in a methyl alcohol solution of one and a-half times the calculated quantity of sodium and heating on the water-bath until the evolution of ammonia ceased. The product was then poured into an evaporating basin, removed from methyl alcohol on the water-bath, and, after dilution, treated with hydrochloric acid. The white precipitate was filtered and crystallised from dilute alcohol, when the characteristic plates of phenylacetic acid were obtained.

The aqueous residue was extracted with ether and the ethereal solution dried and evaporated, when the solid residue on crystallisation from concentrated hydrochloric acid yielded small plates melting at  $124^\circ$  :

0.201 gave 0.2983  $\text{CO}_2$  and 0.0979  $\text{H}_2\text{O}$ .  $\text{C} = 45.17$  ;  $\text{H} = 6.04$ .

$\text{C}_5\text{H}_8\text{O}_4$  requires  $\text{C} = 45.4$  ;  $\text{H} = 6.1$  per cent.

The compound was therefore ethylmalonic acid.

MANCHESTER UNIVERSITY.

CLXXXV.—*Chemical Examination of the Root and Leaves of Morinda longiflora.*

By MARMADUKE BARROWCLIFF and FRANK TUTIN.

Several plants belonging to the genus *Morinda* (Nat. Ord. *Rubiaceae*) have from time to time attracted the attention of chemists, chiefly on account of the tinctorial properties possessed by them. The Indian product "Suranji," which consists of the roots of *M. citrifolia* and *M. longiflora*, was investigated by Anderson (*Annalen*, 1849, **71**, 216),

was obtained from a substance designated "morindin," which, he had, gave a substance of a red compound named "morindone." Subsequent workers have shown that morindin is a glucoside,  $C_{16}H_{12}O_6$ , and that morindone, yielded by its hydrolysis, is hydroxymethylanthraquinone. An exhaustive examination of "Morog Kenda," the root bark of *M. umbellata*, was conducted by Perkin and Hammett (Trans., 1894, **65**, 857), who obtained from it morindin, morindone, and five other anthraquinone derivatives. More recently, Osterle (Arch. Pharm., 1907, **245**, 287) has examined wood of *M. citrifolia*, and obtained from it a dihydroxymethoxyanthraquinone.

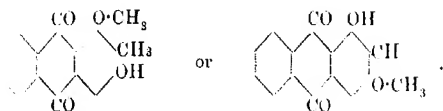
The West African plant, *Morinda longiflora*, G. Don, was brought to our notice by an article in the *Journal of the Society of Arts*, 1903, **53**, 1661, where it is referred to, under the name of "Ojuologbo, Wadly Vine," as one of the most valuable plants of that region, is stated to be used as a medicine by nearly all West African tribes.

Through the kindness of Dr. W. Renner, Medical Officer, Civil Hospital, Freetown, Sierra Leone, we were supplied with a quantity of the roots and leaves of "Ojuologbo," and the identity of the material thus obtained with the products of *Morinda longiflora* kindly confirmed by Mr. E. M. Holmes, F.L.S. A complete botanical description of this plant may be found in the *Flora of Tropical Africa* by F. C. Oliver, F.R.S., Vol. III, p. 192, London, 1877, where it is stated to be known under the native name of "Mbogga."

As a preliminary test, the leaves and root were each examined for the presence of an alkaloid, but with a negative result. The materials were subsequently extracted with alcohol, and the root extract separately investigated.

On examining the extract yielded by the root, no morindone or morindone was obtained, but a quantity of a hydroxymethoxyanthraquinone and a small amount of a monomethyl ether of alkyl were isolated. The root also yielded, in addition to resins and amorphous products, small quantities of formic, acetic, benzoic, palmitic, and citric acids, a little of a phytosterol,  $C_{27}H_{44}O$ , and a considerable amount of a sugar which yielded a diphenyl osazone (see p. 216).

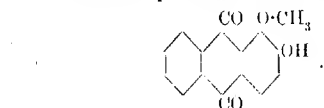
The hydroxymethoxymethylanthraquinone,  $C_{16}H_{12}O_4$ , forms a monoxide when melted at 290°, and gives an acetyl derivative melting at 175°. When heated with 70 per cent. sulphuric acid, it yields a dihydroxy compound identical with the 1:3-dihydroxy-2-methoxyanthraquinone prepared by Schunck and Marchlewski (Trans., 1865, 1826). It must therefore be represented by one of the following formulae:



On heating with hydriodic acid it yields a *dihydroxymethyl-antraquinol*,  $C_{15}H_{12}O_3$  (m. p. 235°), and on methylation gives 1:3-dihydroxy-2-methylantraquinone (m. p. 181°)—a compound which is also easily obtained from the 1:3-dihydroxy-2-methylantraquinone prepared by Schunck and Marchlewski.

The monomethyl ether of alizarin present in "Ojuologbo" root was obtained in needles (m. p. 175°), and yielded an acetyl derivative melting at 209°. It was shown to be identical with the compound of the same nature isolated by Perkin and Hummel (Trans., 1893, 63, 1171) from the root of *Oldenlandia umbellata* ("Chay root").

Alizarin was methylated by Schunck (Mon. Manchester Phil. Soc., 1873), also by Schunck and Marchlewski (*loc. cit.*), and more recently by Gräbe and Aders (*Annalen*, 1901, 318, 369), but the product was, in all cases, a monomethyl ether melting at 228–229°. It was shown by Kostanecki and Dreher (*Ber.*, 1893, 26, 76), that a hydroxyl group in the monohydroxyanthraquinones will not undergo acetylation when it is situated in the 1 position with respect to the carbonyl group, whereas it readily does so when in the 2-, 3-, or 4-position. It was suggested by Schunck and Marchlewski that the hydroxyanthraquinones might show a similar behaviour. They therefore concluded that the monomethylalizarin prepared by them was really the 2-methoxy-compound. This opinion, which was also held by Gräbe and Aders (*loc. cit.*), would lead to the conclusion that the monomethylalizarin occurring in *Morinda longiflora* and *Oldenlandia umbellata* possesses the following formula :



It would appear, however, that the hydroxyanthraquinones, on acetylation, may not always exhibit a behaviour analogous to that of the hydroxyanthraquinones, as it has been shown in this investigation that 1:3-dihydroxy-2-methylantraquinone readily undergoes complete acetylation. It is impossible, therefore, from the above considerations to arrive at a safe conclusion regarding the position occupied by the methoxyl group in the above-described methyl ether of alizarin.

The extract obtained from the "Ojuologbo" leaves differed from that obtained by the root, inasmuch as it contained a considerable proportion of alizarin.

of material which was soluble in petroleum. This petroleum extract yielded palmitic acid, together with traces of acetic and formic acid, and a small amount of the hydrocarbon hentriacontane. The leaves were also found to contain some of the previously-mentioned hydrocarbons, but not the anthraquinone (m. p. 296°), but their most intense constituent is a new, crystalline *alcohol*, which it is proposed to name *micromeritol*. This substance possesses the formula  $C_{20}H_{40}O_4$ , melts at 278°, and has  $[\alpha]_D^{20} + 65.9^\circ$ . It yields *methylmicromeritol*,  $C_{21}H_{42}O_4 \cdot O \cdot CH_3$  (m. p. 116°), on treatment with sodium ethoxide-methyl iodide.

Micromeritol is represented by the same general formula,  $C_nH_{2n+2}O_4$ , as three other crystalline alcohols which have recently been isolated in these laboratories, namely, lippianol,  $C_{25}H_{50}O_4$  (m. p. 300–1°,  $[\alpha]_D^{20} + 64.5^\circ$ ), obtained from *Lippia scaberrima*, Sonder (Power-Tutin, *Arch. Pharm.*, 1907, **245**, 344), and micromerol,  $C_{20}H_{40}O_4$  (m. p. 277–2°,  $[\alpha]_D^{20} + 57^\circ$ ), and micromeritol,  $C_{20}H_{40}O_4$  (m. p. 294–2°,  $[\alpha]_D^{20} + 61.4^\circ$ ), both recently isolated by Drs. F. B. Power and H. S. Day from *Micromeria Chamissonis*. These four substances, moreover, exhibit a marked similarity in properties, and it was therefore appear probable that they are chemically related. Similar compounds appear previously to have been described.

In order to ascertain whether "Ojuologbo" possesses any pronounced physiological action, the following experiments were conducted for us by Mr. H. H. Dale, Director of the Well Physiological Research Laboratories, to whom our thanks are due. Amounts of the extracts corresponding respectively to 17 grams of the dried leaves and to 7.5 grams of the dried root were administered to small dogs, but no definite effects of any kind could be observed.

## EXPERIMENTAL.

### 1. Examination of the Root.

For the purpose of this investigation, a quantity (10.9 kilogram) of the finely-ground root was completely extracted by continuous percolation with hot alcohol. The liquid thus obtained was removed from the greater part of the solvent, the resulting dark brown oil then mixed with water, and distilled with steam until the liquid flowing from the condenser was no longer acid. The distillate contained drops of a heavy, yellow oil possessing a peculiar odor, which was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. The deep red, alkaline liquid thus obtained yielded, on acidification and extraction with ether, a small quantity of a red oil which deposited crystals on standing. The

being separated and recrystallised from alcohol, melted at 45° C., and apparently consisted of palmitic acid.

The ethereal liquid which had been freed from acids by means of sodium carbonate yielded a very small amount of a yellow essential oil. The aqueous portion of the distillate was found to contain formic, acetic, and butyric acids.

The contents of the distillation flask consisted of a quantity of gummy matter, and a dark-coloured, aqueous liquid. The latter was separated from the resin, which was then washed several times with water.

#### *Examination of the Resins.*

The resin was boiled with several successive portions of alcohol, the liquids filtered. In this way there were obtained a dark brown solution, which deposited a small amount of a solid on cooling, and a quantity of an amorphous, brown powder. The latter was very sparingly soluble in alcohol or glacial acetic acid, insoluble in the other usual solvents. Nothing crystalline could be separated from it, and, in view of the possibility of its being a resin, it was submitted to the action of dilute alcoholic hydrochloric acid, but with a negative result.

The solution of that portion of the resins which had been dissolved in alcohol was evaporated on purified sawdust, and treated successively in a Soxhlet apparatus with light petroleum (b.p. 33–50°), ether, chloroform, ethyl acetate, and alcohol.

#### *Petroleum Extract of the Resins.*

This was small in amount. The greater portion of it was soluble in a solution of sodium carbonate, and a further quantity was dissolved by cold aqueous potassium hydroxide. Nothing crystalline was obtained from it.

#### *Ethereal Extract of the Resins.*

This weighed 35 grams. On attempting to redissolve it in ether, it did not readily pass into solution, and this was collected on a filter and independently examined. The ethereal filtrate, containing the more readily soluble constituents of the extract, was shaken with several successive portions of a solution of sodium carbonate, and the aqueous liquids thus obtained, which were all dark red, were examined separately.

*Isolation of a Hydroxymethoxymethylanthraquinone,  $C_{16}H_{12}O_4$* 

On acidifying the first two sodium carbonate extracts, a viscous oil was separated, but the liquids from the subsequent shaking with this alkali yielded a precipitate of a dark yellow solid. This was dissolved in hot alcohol, from which, on cooling, it separated as golden crystals melting at about  $250^\circ$ . As these crystals could not readily be purified, the entire amount of the substance was dissolved in acetic anhydride and the mixture boiled. The resulting acetyl derivative was crystallised from ethyl acetate, when it was obtained in deep yellow needles melting at  $173^\circ$ :

0.1460 gave 0.2824  $CO_2$  and 0.0448  $H_2O$ .  $C = 69.4$ ;  $H = 4.5$ .

0.1652 „ 0.2673  $CO_2$  „ 0.0427  $H_2O$ .  $C = 69.3$ ;  $H = 4.5$ .

$C_{16}H_{12}O_4$  requires  $C = 69.7$ ;  $H = 4.5$  per cent.

The portion of the ethereal extract of the resins which was only sparingly soluble in ether, and which was separated as described above, was found to consist of the substance which yielded this acetyl derivative, as on heating it with acetic anhydride the same product (m. p.  $173^\circ$ ) was obtained.

The pure acetyl derivative was hydrolysed, and the product crystallised from absolute alcohol. It separated in golden yellow needles melting at  $290^\circ$ :

0.1965 gave 0.2780  $CO_2$  and 0.0444  $H_2O$ .  $C = 71.1$ ;  $H = 4.6$ .

0.1142 „ 0.2291  $CO_2$  „ 0.0463  $H_2O$ .  $C = 71.5$ ;  $H = 4.5$ .

$C_{16}H_{12}O_4$  requires  $C = 71.6$ ;  $H = 4.5$  per cent.

No substance of the formula  $C_{16}H_{12}O_3$  and possessing properties agreeing with those of this compound has hitherto been described. The methoxyl determination by means of Perkin's modification of Zeisel's method gave the following result:

0.2585 gave 0.2275 AgI.  $CH_3 \cdot O = 11.6$ .

$C_{16}H_{12}O_3 \cdot O \cdot CH_3$  requires  $CH_3 \cdot O = 11.6$  per cent.

The flask which had been employed in this estimation contained, together with the hydriodic acid, a quantity of a solid substance. This was collected, and crystallised from ethyl acetate, when it was obtained in dark yellow needles melting at  $235^\circ$ :

0.1050 gave 0.2802  $CO_2$  and 0.0416  $H_2O$ .  $C = 74.2$ ;  $H = 4.8$ .

$C_{17}H_{12}O_2$  requires  $C = 75.0$ ;  $H = 5.0$  per cent.

A further quantity of this substance (m. p.  $235^\circ$ ) was prepared by oxidising with chromic acid, when a compound was obtained which crystallised from ethyl acetate in deep golden leaflets melting at  $26^\circ$ . The latter substance was also produced, and in much better yield,

the original methoxy-derivative with 70 per cent. sulphuric acid. It was analysed with the following result:

0.855 gave 0.2290 CO<sub>2</sub> and 0.0325 H<sub>2</sub>O. C = 70.6; H = 4.1.

C<sub>15</sub>H<sub>10</sub>O<sub>4</sub> requires C = 70.9; H = 3.9 per cent.

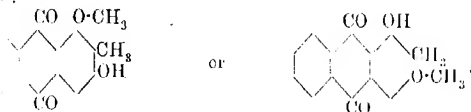
The compound agrees in composition and properties with the 1:3-dihydroxy-2-methylantraquinone prepared by Schunck and Marchlewski (Trans., 1894, 65, 182), and is evidently identical with it.

In order to confirm this conclusion the acetyl derivative was prepared, and was obtained in slender, pale yellow needles melting at 290°, the temperature recorded by Schunck and Marchlewski for the melting point of the acetyl derivative of the substance prepared by them.

0.1298 gave 0.2992 CO<sub>2</sub> and 0.0462 H<sub>2</sub>O. C = 67.5; H = 4.2.

C<sub>15</sub>H<sub>8</sub>O<sub>4</sub>(CO·CH<sub>3</sub>)<sub>2</sub> requires C = 67.5; H = 4.1 per cent.

The yellow substance melting at 290°, isolated from the root of *Morinda longiflora*, must, therefore, be a *hydroxymethoxymethylantraquinone* possessing a constitution represented by one of the following formulae:



The compound, C<sub>15</sub>H<sub>12</sub>O<sub>3</sub> (m. p. 235°), which was formed from this monomethoxymethylantraquinone by the action of hydriodic acid, and which yielded 1:3-dihydroxy-2-methylantraquinone on oxidation, must, therefore, be a *dihydroxymethylanthrone*.

*3-Dimethoxy-2-methylantraquinone*.—On solution in alcohol and treatment with sodium ethoxide and methyl iodide, the hydroxymethylantraquinone yielded 1:3-dimethoxy-2-methylantraquinone. This new compound is also readily produced in a similar manner from 1:3-dihydroxy-2-methylantraquinone. It crystallises in golden-coloured needles melting at 181°:

0.1112 gave 0.3020 CO<sub>2</sub> and 0.0537 H<sub>2</sub>O. C = 72.1; H = 5.2.

C<sub>17</sub>H<sub>14</sub>O<sub>4</sub> requires C = 72.3; H = 5.0 per cent.

#### *Isolation of a Monomethyl Ether of Alizarin.*

The oily product which separated on acidifying the first two alkaline extracts obtained by shaking the ethereal solution of the readily-soluble portion of the ether extract of the resins with sodium carbonate, as already described, deposited no solid on standing. It was, however, thought probable that it might contain some of the above-described hydroxymethoxymethylantraquinone, or other



phenolic substance, together with carboxylic acids. It was then heated with acetic anhydride, the product dissolved in ether, and the ethereal liquid shaken with a solution of sodium carbonate. Addition of the dark-coloured alkaline liquid thus obtained yielded a viscid substance from which nothing crystalline could be separated, but on evaporating the ethereal solution containing the non-acidic, acetylated product an oily liquid was obtained which deposited a small quantity of a solid on standing. This was collected and after several crystallisations from ethyl acetate, was obtained as pale yellow needles melting sharply at  $209^{\circ}$ . It was hydrolysed with alcoholic potash, and the product crystallised from ethyl acetate, where it formed yellow needles melting at  $175^{\circ}$ . Unlike its acetyl derivative, this substance is freely soluble in alcohol.

On dissolving a trace of this compound in concentrated sulphuric acid a brownish-red colour was produced, which, on heating the liquid to  $150^{\circ}$ , changed to an intense red. It dissolved in a solution of barium hydroxide with a red colour, and on boiling the liquid, some time a violet-coloured precipitate was deposited. The substance, melting at  $175^{\circ}$ , was analysed with the following result:

0.0629 gave 0.1638  $\text{CO}_2$  and 0.0228  $\text{H}_2\text{O}$ .  $\text{C} = 71.0$ ;  $\text{H} = 4.0$ .  
 $\text{C}_{15}\text{H}_{10}\text{O}_4$  requires  $\text{C} = 70.9$ ;  $\text{H} = 3.9$  per cent.

The composition and properties of this substance agree with those of the monomethyl ether of alizarin which was isolated by Perkins and Hummel (Trans., 1893, 63, 1174) from the root of *Oldenlandia umbellata*, Linn. ("Chay root"),—a plant belonging to the same natural order (*Rubiaceae*) as *Morinda longiflora*. Unfortunately, sufficient material was not available to permit of our making a methoxyl determination. The melting point found by Perkins and Hummel for the compound isolated by them is  $3^{\circ}$  higher than that found for our substance, but the acetyl derivative of our preparation melts at  $209^{\circ}$ . No doubt can therefore be entertained regarding the identity of the above-described substance,  $\text{C}_{15}\text{H}_{10}\text{O}_4$ , with the monomethyl ether of alizarin obtained from "Chay root".

The oily liquid, from which the acetyl derivative of the monomethyl ether of alizarin had been separated, was hydrolysed. The product yielded a further quantity of the hydroxymethoxymethyl anthraquinone, but no other solid substance could be obtained from it.

After the ethereal solution of the readily soluble portion of the ether extract of the resins had been treated with a solution of sodium carbonate, as already described, it was shaken with a dilute solution of sodium hydroxide. The product which separated on acidifying the alkaline liquid thus obtained was only small in amount and nothing crystalline could be obtained from it. The ethereal

which was now free from substances of an acidic or phenolic nature, was evaporated, when a product was obtained which deposited a solid on standing. This was several times crystallised from alcohol, and obtained in colourless leaflets melting at  $130^{\circ}$ . On treatment with acetic anhydride and sulphuric acid, it gave the color reaction characteristic of the phytosterols. After drying at  $100^{\circ}$  it was analysed:

0.0828 gave 0.2533  $\text{CO}_2$  and 0.0889  $\text{H}_2\text{O}$ . C = 83.4; H = 11.9.

$\text{C}_{27}\text{H}_{46}\text{O}$  requires C = 83.9; H = 11.9 per cent.

#### *Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resins.*

The chloroform extract of the resins was small in amount, and yielded only a little of the above-described hydroxymethoxymethylanthraquinone.

The portion of the resins which was extracted by ethyl acetate amounted to 22 grams. Various attempts were made to obtain a crystalline substance from it, but without success.

The remainder of the resins, which was soluble only in alcohol, is the largest extract obtained, and amounted to 90 grams. Although submitted to a prolonged investigation, it yielded nothing crystalline.

#### *Examination of the Aqueous Liquid.*

The combined aqueous liquid and washings, which had been separated from the resins, as previously described, were filtered, and extracted five times with ether. The ethereal liquid was then shaken with six successive small portions of a solution of sodium carbonate. On acidifying the first alkaline liquid thus obtained, a thick, oily product was precipitated, which did not solidify, but the subsequent extracts gave a yellow solid, which was found to consist of the hydroxymethoxymethylanthraquinone previously isolated from the resins.

The aqueous liquid which had been extracted with ether was shaken with a solution of barium acetate until no further precipitate was formed, then filtered, and the precipitate washed. This precipitate was examined, but nothing crystalline was obtained from it. A slight excess of a solution of basic lead acetate was added to the filtrate from the barium precipitate, the resulting soluble lead compounds collected, washed, suspended in water, decomposed by means of hydrogen sulphide, and the liquid filtered. The filtrate was concentrated, mixed with purified sawdust, and dried, after which it was extracted with various solvents. From the portion removed by means of ether, a solid was obtained which,

after crystallisation from ethyl acetate, melted at  $151-152^{\circ}$  and gave the reactions of anhydrous citric acid.

The filtrate from the lead acetate precipitate was freed from lead and concentrated. It was found to contain a large amount of hexose, as it readily yielded *d*-phenylglucosazone melting at  $216^{\circ}$ .

### 11. *Examination of the Leaves.*

The ground leaves (5.8 kilograms) were completely extracted by continuous percolation with hot alcohol, the liquid concentrated, and the residual dark green extract mixed with water and distilled on steam. The distillate, on extraction with ether, gave a small amount of an essential oil possessing an unpleasant odour, and the aqueous liquid from which this had been removed was found to contain formic, acetic, and butyric acids.

This distillation flask then contained a quantity (135 grams) of dark green resin, which was separated from the aqueous liquid, well washed with hot water.

### *Examination of the Resins.*

The resinous mass was dissolved in alcohol, the solution mixed with purified sawdust, and the mixture dried, after which it was extracted successively in a Soxhlet apparatus with light petroleum (b. p.  $33-56^{\circ}$ ), ether, chloroform, ethyl acetate, and alcohol.

### *Petroleum Extract of the Resins.*

The petroleum extract amounted to 59 grams. It was dissolved in ether and the resulting liquid extracted successively with solution of sodium carbonate and potassium hydroxide. The products obtained by this treatment were small, and yielded nothing definite, although the liquid obtained on shaking with the latter alkali had a violet colour.

The ethereal solution was then evaporated, the residue dissolved in an alcoholic solution of potassium hydroxide, and the mixture heated for two hours. The greater part of the alcohol was removed, water added, and the alkaline liquid extracted with oil. The ethereal liquid thus obtained yielded, on evaporation, a small product, which was distilled under diminished pressure. The distillate deposited a solid on standing which, when crystallised in ethyl acetate, formed leaflets melting at  $68^{\circ}$ :

0.0816 gave 0.2551  $\text{CO}_2$  and 0.1085  $\text{H}_2\text{O}$ .  $\text{C} = 85.3$ ;  $\text{H} = 14.8$ .

$\text{C}_{31}\text{H}_{64}$  requires  $\text{C} = 85.3$ ;  $\text{H} = 14.7$  per cent.

This substance was therefore the hydrocarbon hentriacontane.

liquid from which this hydrocarbon had been separated appeared to contain oxygenated substances, probably alcohols, but gave no reaction for phytosterol.

The alkaline liquid from which the hydrocarbon had been removed by means of ether was acidified, and distilled with steam. This yielded a little acetic and formic acids. The contents of the distillation flask were then shaken with ether, the ethereal liquid filtered, concentrated to a small bulk, and a considerable volume of petroleum added. This caused the precipitation of a quantity of resin, from which the petroleum liquid was decanted. The ether was then evaporated and the residue distilled under diminished pressure. The distillate, which solidified on cooling, was crystallized from methyl alcohol, when it yielded a product melting at  $60^{\circ}$ ;

0.1053 gave 0.2906  $\text{CO}_2$  and 0.1152  $\text{H}_2\text{O}$ .  $\text{C} = 75.3$ ;  $\text{H} = 12.2$ .

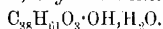
$\text{C}_{16}\text{H}_{32}\text{O}_2$  requires  $\text{C} = 75.0$ ;  $\text{H} = 12.5$  per cent.

It, therefore, consisted largely of palmitic acid.

#### *Ethereal Extract of the Resins.*

This was a soft, green mass weighing 57 grams. On treating with a limited amount of ether, a quantity of a green solid remained undissolved, and was collected on a filter. The ethereal filtrate was then shaken with a solution of sodium carbonate. The alkaline liquid thus obtained yielded, on acidification, a product which appeared to consist to a considerable extent, of the hydroxymethoxymethylanthranilate previously isolated from the root, but it could not be purified. After extracting the ethereal liquid with sodium carbonate solution, it was washed with water, when a large quantity of chlorophyll was removed, and subsequent extraction with potassium hydroxide yielded a further quantity of a similar, uncrystallisable product. The ethereal liquid finally left on evaporation only a soft, green resin.

#### *Isolation of a New, Crystalline Alcohol, Morindanol,*



The above-mentioned sparingly soluble solid was dissolved in a considerable quantity of hot alcohol and the solution digested with animal charcoal, by which means the greater part of the green colour was removed. On concentrating the solution, an amorphous, slightly green product was obtained, which melted from  $240^{\circ}$  to  $270^{\circ}$ . This was again dissolved and treated with animal charcoal, which removed the last traces of colour, when, after repeated fractionations from charcoal, the greater part of it was obtained in colourless, glistening needles melting at  $278^{\circ}$ . The substance, after drying at  $100^{\circ}$ , was obtained:

# LABORATORY CHEMICAL EXAMINATION OF MORINDA LONGIFLORA.

0.4077 gave 0.3083  $\text{CO}_2$  and 0.1041  $\text{H}_2\text{O}$ .  $\text{C}=78.2$ ;  $\text{H}=10.7$ .  
 $\text{C}_{12}\text{H}_{14}\text{O}_4$  requires  $\text{C}=78.3$ ;  $\text{H}=10.7$  per cent.

The anhydrous substance gave the following result:

0.1025 gave 0.2852  $\text{CO}_2$  and 0.0978  $\text{H}_2\text{O}$ .  $\text{C}=75.9$ ;  $\text{H}=10.6$ .  
 $\text{C}_9\text{H}_{10}\text{O}_4 \cdot \text{H}_2\text{O}$  requires  $\text{C}=76.0$ ;  $\text{H}=10.7$  per cent.

0.3808, dissolved in 100 c.c. of absolute alcohol, gave  $\alpha_D + 0.68$  in a 2 dm. tube, whence  $[\alpha]_D^{20} + 65.9^\circ$ .

The composition and properties of this substance do not agree with those of any compound previously described, and, being of an alcohol nature, it is proposed to designate it *morindanol*.

If a small quantity of morindanol is dissolved in alcohol, and ammonia added, no precipitate is produced on diluting the solution with water, even if the greater part of the alcohol has previously been evaporated. The clear liquid thus obtained seems to have the character of a colloidal solution, as no morindanol will separate from it until an aqueous solution of an electrolyte is added, and, on allowing it to stand, it forms a perfectly transparent jelly.

*Methylmorindanol*,  $\text{C}_{12}\text{H}_{14}\text{O}_3 \cdot \text{O} \cdot \text{CH}_3$ .—A quantity of morindanol was dissolved in alcohol, sodium ethoxide and methyl iodide added, and the mixture heated for three hours. The product was then dissolved in ether and freed from unchanged material by means of potassium hydroxide. The *methylmorindanol* was crystallised from alcohol, and it formed rosettes of needles which melted at  $116^\circ$ . This substance contained no solvent of crystallisation. A methoxyl determination gave the following result:

0.1951 gave 0.0165 AgI.  $\text{CH}_3 \cdot \text{O}=5.2$ .

$\text{C}_{12}\text{H}_{14}\text{O}_3 \cdot \text{O} \cdot \text{CH}_3$  requires  $\text{CH}_3 \cdot \text{O}=5.2$  per cent.

*Oil of Lemons, Ethyl Acetate, and Alcohol Extracts of the Resins*.—These were all small in amount, and nothing crystalline could be obtained from any of them.

## *Examination of the Aqueous Liquid.*

The aqueous liquid obtained from the extract of the leaves, as previously described, was examined in a manner similar to that recorded in connexion with the corresponding product from the root, with the exception that the treatment with barium acetate was omitted. A further quantity of the hydroxymethoxymethylanthraquinone (0.1220) was obtained, and the aqueous liquid, after purification by means of basic lead acetate, yielded *D*-phenylglucosazone melting at  $211^\circ$ . No citric acid could be obtained from the leaves.

THE WELDON CHEMICAL RESEARCH LABORATORIES,  
 LONDON, E.C.

XXXVI.—*The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide. Part II. The Constitution of the Products.*

By ARTHUR LAPWORTH and ELKAN WECHSLER.

In the previous paper (Trans., 1907, 91, 978), it was shown that amyl cyanodihydrocarvone in presence of sodium ethoxide converts cyanodihydrocarvone into a substance (*L*),  $C_{11}H_{14}O_2N_2$ , which proved to be the lactam of an amino-acid (*A*),  $C_{10}H_{13}ON(NH_2) \cdot CO_2H$ . By the action of dilute acids on either of these, there were obtained an isomeric acid (*L*) and two isomeric lactonic bases (*B* and *B'*), to which the common formula  $C_{10}H_{14}ON(NH_2) \cdot CO$  was assigned (*loc. cit.*, p. 978).

The prolonged action of acids on the base (*B*) led to the formation of a substance which, although capable of forming salts with bases and expelling carbon dioxide from carbonates, was not carboxylic in character: this was referred to as "the lactonic acid," and was given the formula  $C_{10}H_{16}O_2N(OH) \cdot CO$ . From this substance, 2:3:6-tri-

hydrobenzoic acid was obtained by long-continued heating with concentrated hydrochloric acid.

The present paper contains an account of the experiments on the lactonic acid which led us to believe that it did not owe its acid properties to the presence of a carboxyl group, and also the results which we venture to believe establish the ultimate constitution of the several compounds mentioned above.

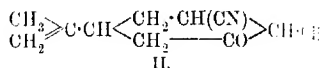
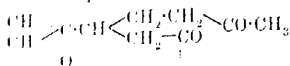
In discussing the latter question, we may recall the fact that there is strong evidence in favour of the view that the  $NH_2$  group is not in the amino-acid and in the base *B*. This we have since been able fully to confirm by preparing the *benzylidene* derivative,  $H_{14}ON(N:CHPh) \cdot CO$ , of the base by warming the latter with

aldehyde in absence of any solvent.

Respect to the ultimate constitution of the above compounds was gained on an examination of the products formed when they are acted on by ferrous hydroxide in presence of alkalis. This treatment, even the cold, leads to their decomposition, ammonia being evolved, and the iron is converted into the ferric state (compare Trans., 97, 91, 980). In the case of "the lactonic acid," there is also formed a neutral compound having the formula  $C_{10}H_{16}O_3$ , which was found to be lactonic in character and to contain the group  $:C \cdot CO \cdot CH_2$ ; this substance yielded iodoform with iodine and alkali; on oxidation, it

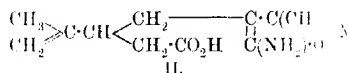
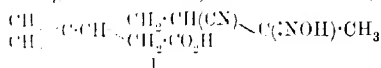
was converted into terpenylic acid, and was identical with *d*-methylethylheptanonolide, although in certain particulars its properties are not precisely those assigned by Baeyer to that substance.

A comparison of the formula of methylethylheptanonolide



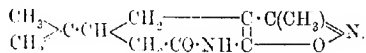
with that of cyanodihydrocarvone (II) shows at once that the process leading from the latter to the former involves scission of the dihydrocarvone ring between the CH and CO groups. This can only be explained by assuming that the attack of the amyl nitrite on cyanodihydrocarvone was directed at that point and not at the  $\text{CO} \cdot \text{CH}_2$  group, as is usually the case when a ketone reacts with an ester in presence of sodium ethoxide.

Experiments with other cyclic ketones containing the group  $\text{CH} \cdot \text{CO} \cdot \text{CH}_2$  have shown us that such is their normal behaviour in nitrous esters; in the cases we have examined, the first product on treatment with water yields an open-chain hydroximinic acid, when acids are used as catalytic agents. A similar change in the case of cyanodihydrocarvone would lead to the production of the acid having the structure (I):



This substance, however, as the oxime of a  $\beta$ -cyanoketone, would readily be converted into an "isooxazolinimide," to which, for reasons which follow, the amino-structure (II) may be adopted.

The free acids here depicted, however, require for their formation the absorption of water; this, however, is absent during the reaction, so that, instead of the free acid, the formula of which has just been given and which represents the amino-acid (*d*), the anhydride or lactam is produced:



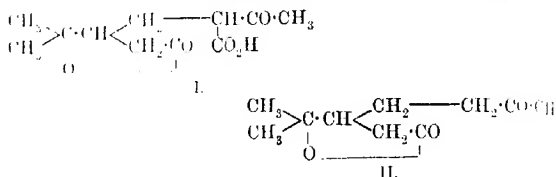
There seems no reason whatever to doubt that this structure (L) represents the compound referred to as the lactam (*L*). The well-defined acid character of that substance is explained by the presence





lone" or hydroxy-isooxazole. That we definitely adopted the hydroxy- rather than the carbonyl formula for the "isooxazolone" residue, is because the balance of evidence generally appears in favour of this in the cases previously studied, and also because the amino- and lactonic substructures for the allied acid (*A*) and the lactonic base (*B*) seems to have been definitely established by the experiments already described.

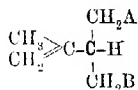
The reduction of the lactonic acid occurs in accordance with the usual behaviour of isooxazolones. We have more recently found that the acid, as well as the compounds from which it is obtained, namely hydroxylamine and methoethylheptanonolide when heated for a considerable time with dilute acids. Doubtless the reaction which now consists, in the first instance, of the formation of hydroxylamine, and the acid (*A*), which, being a  $\beta$ -ketoic acid, loses the elements of  $\text{CO}_2$



anhydride with formation of the ketone (II).

It is interesting that the isomeric lactonic base (*B'*), when heated with dilute acid, yields racemic methoethylheptanonolide. This is in line with the fact that the rotatory power previously assigned to the base (*B*) (*loc. cit.*, p. 987) was very close to that of the base which led us to re-examine the former, with the result that it was found to be totally inactive, and the rotation given in the first paper was doubtless that of a specimen of the active base (*B*).

The two lactonic bases therefore represent the active and racemic forms respectively, so that the action of mineral acids on the lactonic (*L*) leads to a partial inversion of the asymmetric grouping:



For active methoethylheptanonolide, in which the unsaturated  $\beta$ -carbon is absent, does not racemise under similar and more violent conditions. Thus the group  $\text{C}(\text{CH}_2)$  functionates in the same way as the carbonyl or cyano-group when attached at the same time as hydrogen to an asymmetric carbon atom.

The constitution of the substance described in the former paper as the isomeric lactam (*L'*) remains obscure. It appears to be an active

the substance in the formation of the inactive lactonic base (*B'*), but a very high dextrorotatory power,  $[\alpha]_D$  being greater than +200. Such characters as might be expected in a stereoisomeride of lacton (*L*), but a satisfactory formula indicating this as well as different optical activity cannot be devised, so that the difference is probably a structural one, but we have no further evidence to cite.

#### EXPERIMENTAL.

##### *Action of Bromine on the Lactonic Acid.*

A solution of bromine in glacial acetic acid was added to one of the lactonic acids in the same solvent, containing excess of sodium acetate. The colour of the halogen at first rapidly disappeared, and when this had gone to be the case the liquid was diluted with water; the solid separated being collected and purified by crystallisation from alcohol.

0.142 gave 0.2533 AgBr. Br = 26.21.

$C_{11}H_{10}O_5NBr$  requires Br = 26.25 per cent.

The substance obtained in this way separates from solvents in colourless crystals which melt and decompose at 153°.

The bromo-derivative exhibits few of the characteristics of the lactonic compound, being insoluble in alkalis and affording none of the colour reactions so characteristic of the lactonic acid.

##### *Oxidation of the Lactonic Acid.*

Oxidation of the acid in excess of sodium carbonate or hydroxide rapidly discharges the colour of potassium permanganate or ferric chloride and a neutral oxidation product separates. The formation of this compound is not accompanied by that of any compound of low carbon content, so that it may be regarded as certainly containing the carbon atoms of the original lactonic acid.

The oxidation product appears to be very sensitive to oxidising agents in alkaline media, and is therefore more satisfactorily prepared by the use of solutions of the lactonic acid in dilute sulphuric acid and potassium dichromate as oxidising agent. Quantitative experiments showed that the formation of the compound involves the intervention of one molecule of the lactonic acid and one atom of oxygen.

The substance was purified by crystallisation from alcohol:

0.2731 gave 0.5780  $CO_2$  and 0.1558  $H_2O$ . C = 57.7; H = 6.3.

0.257 g. gave 7.5 c.c. of moist nitrogen at 11° and 768 mm. N = 6.6. The composition of this substance cannot be expressed by a simple formula, but agrees fairly well with that of a compound of high molecular weight, derived from the lactonic acid by oxidation and

subsequent removal of water. The compound having the composition  $C_4H_5NO \cdot 6H_2O$  requires  $C=58.0$ ;  $H=5.9$ ;  $N=6.2$  per cent. The physical characters of the substance and its almost amorphous nature lend probability to this view.

The condensation product is insoluble in water, but dissolves sparingly in carbon tetrachloride, benzene, or ether, and readily in most of the commonly used organic media.

It is acted on slowly by cold dilute mineral acids, and rapidly by concentrated acids, giving intensely blue solutions. With concentrated acid, it yields yellow solutions which turn blue when diluted with water. These blue solutions turn yellow on addition of excess ammonia, but when reacidified they gradually regain the original colour.

#### *Action of Sodium Hydroxide and Ferrous Hydroxide on the Lactonic Acid.*

When a solution of the sodium salt of the lactonic acid in excess of alkali is shaken with freshly precipitated ferrous hydroxide, the green colour of the latter gradually disappears, while the odour of ammonia is almost at once made perceptible. In order to obtain reduction products, 18 grams of the acid were dissolved in 600 c.c. of sodium hydroxide, and to this was then added 36 grams of ferrous chloride dissolved in about 350 c.c. of water, the whole being heated to boiling until the odour of ammonia was no longer perceptible, a process which required about one hour. The iron hydroxides were then removed by filtration, extracted repeatedly with boiling water, and the united filtrates evaporated to 200 c.c., cooled, mixed with 30 c.c. of concentrated hydrochloric acid, and extracted with benzene. The latter, on evaporation, left an oil which finally set to a hard crystalline mass, weighing 13.2 grams, or 96 per cent. of the calculated amount:

0.6350 gave 0.7978  $CO_2$  and 0.2594  $H_2O$ .  $C=64.9$ ;  $H=8.6$ .

$C_4H_5O_3$  requires  $C=65.2$ ;  $H=8.7$  per cent.

The substance crystallised from water in needles or plates melting at  $47-48^\circ$ , and boiled without decomposition about  $300^\circ$ .

0.5252, made up to 20 c.c. with absolute alcohol at  $15^\circ$ , gave rotation of  $+5.10$ , whence  $[\alpha]_D^{20} +59.0$ .

It was neutral to litmus, but exhibited the lactonic character of the acid from which it had been prepared. 0.3939 gram, after boiled with 25 c.c. 0.98 *N*-sodium hydroxide, partly neutralised the latter so that after fifteen minutes only 3.4 c.c. *N*.10-sulphuric acid was required for neutralisation. The equivalent found was 187, as required for a lactone,  $C_4H_5O_3$ , being 184.

The substance was also ketonic in character, yielding precipitates with solutions of phenylhydrazine acetate and semicarbazide acetate, and a haloform on treatment with iodine and alkali, indicating that it contained the ketonic group  $\text{C}=\text{CO}\cdot\text{CH}_3$ .

Baeyer has described a substance having the above formula, and which contains the groupings shown to be present in the substance under notice. Baeyer's compound was obtained by oxidising isosaxterpan (*Ber.*, 1898, **31**, 3216), and it was assigned the melting point  $48-49^\circ$ , but the rotation of its 13 per cent. alcoholic solution corresponded with  $[\alpha]_D +44.4$ . The substance was methoxyheptanonolide, which has also been described by Jodlerowski (*Contr.*, 1899, **i**, 1241), according to whom the melting point is  $48^\circ$  and  $[\alpha]_D +55.3$  in alcoholic solution.

In view of these discrepancies, we undertook the oxidation of the ketone obtained by us, employing the method used by Wallach (*Ber.*, 1893, **277**, 118). From 2 grams of the methyl ketone, 0.7 grams of an acid were obtained, which melted at  $57^\circ$  in the solid condition and at  $90^\circ$  when anhydrous, was inactive, and had the properties of terpenylic acid:

0.278 g. gave 0.7002  $\text{CO}_2$  and 0.2531  $\text{H}_2\text{O}$ .  $\text{C} = 50.3$ ;  $\text{H} = 7.1$ .

$\text{C}_8\text{H}_{12}\text{O}_4\cdot\text{H}_2\text{O}$  requires  $\text{C} = 50.6$ ;  $\text{H} = 7.1$  per cent.

The substance obtained by reducing the lactonic acid is therefore probably methoxyheptanonolide. In all probability, it is thus obtained in a high state of purity, and possibly the low rotatory power noted by Baeyer (*loc. cit.*) was due to the presence of some quantity of the inactive ketone in his specimen.

#### *Preparation of d-Methoxyheptanonolide by the Action of Acids on the Lactonic Base (B).*

During the preparation of the lactonic acid from the lactonic base (*B*) (*loc. cit.*, 1907, **91**, 989), indications of the occurrence of a secondary reaction were frequently obtained, a slow evolution of carbon dioxide being observed; moreover, the yield of lactonic acid never exceeded 50 per cent. of that theoretically possible, and the mother liquor invariably showed powerful reducing properties similar to those of a solution of hydroxylamine. The presence of the latter substance was easily established by converting it into impure acetoxime with acetic acid and alkali, hydrolysing the extracted oxime with hydrochloric acid, and thus obtaining hydroxylamine hydrochloride free from organic matter.

In purifying the mother liquor for the above purpose, it was noticed that when it was shaken with benzene, a further separation of the lactonic acid took place, and on examining the benzene extract the following results were obtained:

latter was found to yield an oil which slowly crystallised; the product thus obtained was found to be *d*-methoethylheptanonolide in state approaching purity. After the complete removal of the substances, extraction of the mother liquor with chloroform leads to recovery of a further quantity of the lactonic acid.

In this way, from 36 grams of the lactonic base, 22 grams of the lactonic acid and 7.4 grams of the methyl ketone were obtained, representing 80 per cent. of the theoretical amount.

*Formation of Racemic Methoethylheptanonolide by the Action of Dilute Acids on the Racemic Isomeric Lactonic Base (B).\**

In the hope of throwing light on the question of the relation between the bases (*B*) and (*B'*) (Trans., 1907, 91, 985 and 987), hydrolysis of the latter was undertaken. The substance was heated for five hours with about fifteen times its weight of *N*-sulphuric acid, and afterwards with excess of sodium hydroxide and ferrous hydroxide until ammonia ceased to be evolved. The filtered and evaporated solution was then acidified and extracted with chloroform, which removed a considerable quantity of an oil. This rapidly solidified on cooling, and the resulting material was crystallised from ether, from which it separated in colourless needles melting at 63°. It was optically inactive, and was identical in all respects with the *d*-methoethylheptanonolide described by Tiemann and Semmler (*Ber.*, 1885, 28, 1778).

*Benzylidene Derivative of the Base (B).*

Equimolecular proportions of the lactonic base (*B*) (Trans., 1907, 91, 980) and benzaldehyde were treated together on the water-bath for three hours. The product when cool became crystalline on filtration with alcohol, and was purified by repeated crystallisation from that solvent:

$d_{20}^{25.8}$  gave 23.8 vol. moist nitrogen at 18° and 756 mm.  $N = 22$   
 $C_{15}H_{22}O_3N_2$  requires  $N = 20.0$  per cent.

The compound crystallises from alcohol in almost colourless crystals which melt at 120°, forming a yellow liquid. It dissolves somewhat readily in benzene, acetone, chloroform, or acetic acid, more sparingly in ether, carbon tetrachloride, carbon disulphide, or cold alcohol. It is insoluble in dilute acids or alkalis. When boiled with water, especially in presence of acids, it is resolved into its components.

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\* This substance was previously stated to be active (compare p. 1922).

XXXVII.—*The Synthesis of Acridines and Phenonaphthacridines: Tetra- and Hexa-methylacridines: Dimethylphenonaphthacridines: Dicyllylmethylene-diamines.*

By ALFRED SENIER and ARTHUR COMPTON.

FROM the simplest acridine obtained by the condensation of methylene chloride with arylamines was hexamethylacridine. The extension of this method to the synthesis of simpler acridines seemed probable, although the reaction had already been studied by several investigators. (For references, compare Senier and Goodwin, *Trans.*, 1907, **81**, 280.) With this object in view, we re-investigated the reaction between methylene chloride and the xylidines, and succeeded in obtaining two tetramethylacridines. Eventually the scope of our enquiry widened into a more general study of the synthesis of acridines and phenonaphthacridines. The following methods of synthesis were employed:

1. Condensation of aryl- or naphthyl-amines or mixtures of them with methylene di-iodide (Senier and Goodwin, *loc. cit.*), or methylene dichloride (Senier and Austin, *Trans.*, 1906, **89**, 1390).
2. Condensation of mixtures of arylamines and phenols or naphthols with methylene di-iodide (Senier and Austin, *Trans.*, 1907, **91**, 1240), or methylene dichloride.

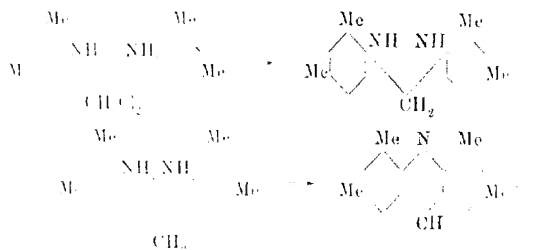
3. Condensation of diarylmethylene-diamines with an arylamine and methylene dichloride (Ullmann and Waitz, *Ber.*, 1903, **36**, 1019).

From *m*-4-xylidine and *p*-xylidine and the analogous xylenols by the above methods, we obtained the corresponding dicyllylmethylene-diamines and tetramethylacridines. *p*-Nylidine gave a diamine but no acridine by the first method; but the desired acridine was obtained from the diamine by the third and also by the second method from the xylidine and xylenol. Improvements were made in the preparation of 6:11, 6:7:9-hexamethylacridine (Senier and Goodwin, *loc. cit.*) by the first method, using methylene di-iodide, and it was found that by use of methylene dichloride the same base could be prepared. *ac*-1:3-Naphthols with each of the xylidines gave by the second method the corresponding dimethylphenonaphthacridines, one of which Ullmann (*Chem. Centr.*, 1901, **2**, 568) has already described as resulting from the interaction of formaldehyde and a mixture of xylidine and naphthol. The experiments of Senier and Austin (*loc. cit.*) showed that the first method was not a promising one for the synthesis of phenonaphthacridines, and it was therefore not used. Next, we found that the xylenol and naphthylamine could not

replace the isophthalal and xylylidine, for, in an experiment using isophthalal and a diphenylamine only,  $\alpha$ -N<sup>a</sup>- $\beta$ -dinaphthaeridine was obtained.

The inability of *p*-xylylidine to condense directly to an acridine by the first method, in spite of repeated attempts to effect the reaction, appears to be due to the absence of a methyl group in the para-position with respect to the amino-group. For, excluding the alkyl substituents in the meta-position, every alkyl derivative of acridine discovered by the first method, or by the analogous method in which formaldehyde is used, contains an alkyl in a para-position with respect to the nitrogen linking. Further, if it be assumed that the method referred to a methylenediamine is first formed (without an intermediate methylenearylamine), it may well undergo methylenediazidine metastasis observed in the case of toluidine (Eberhardt and Welter, *Ber.*, 1891, 27, 1804) before the final condensation to acridine takes place. In this event, only those arylamines which contain alkyl groups in para-positions with respect to their amino-groups can form such methylenediamines as are capable of being metastasized into diaminodiarlylmethanes in which the amino-groups arrange themselves in an ortho-position with respect to the methyl group. In all other cases, the formation of acridines is excluded, and, by the benzidine metastasis, *pp*-diaminodiarlylmethanes would be formed.

Thus, in the case of *m*-1-xylylidine, the course of the changes would



That diaminodiarlylmethanes are formed when formaldehyde or other analogues is used, and that they condense to acridines, is shown by the experiments of Meyer and Gross (*Ber.*, 1893, 32, 221), Ullmann and Marié (*Ber.*, 1901, 34, 4367), Haase (*Ber.*, 1902, 35, 388), and Ullmann (*Ber.*, 1903, 36, 1017).

The third method was used by Ullmann and Waitz in the preparation of 5:7-dimethylacridine from di-*p*-tolylmethylenediamine and a mixture of *p*-toluidine and its hydrochloride. The reaction is of

to the third one described by Ullmann and Naef (*Ber.*, 1900, 33, 4). That by the first method, *m*-4-xylylene yields an acridine, while *m*-4-xylylene does not, we have explained by the metastasis which intermediate diamines formed undergo. Now by the third method, which the starting point is the diamine, that the diamines derived from *m*-4-xylylenes yield acridines, indicates that when this method is used no metastasis take place; for, whilst the diaminodiphenylamine derived by metastasis from the 1:3:4-diamine might give an acridine by this method, the corresponding compound from the 1:3:5-diamine could not do so. In both cases, therefore, it is shown that substitution with condensation takes place directly between the arylamine and the methylenediamine.

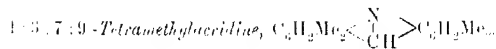
*Condensation of m-4-Xylylene with Methylene Dichloride.*

When *m*-4-xylylene (2 mols.) and methylene dichloride (1 mol.) are sealed in a closed tube at 160–170° for three hours, or at a somewhat higher temperature for a shorter period, the chief product is the corresponding dixylylmethylenediamine, identical with that described by Senior and Goodwin (*Trans.*, 1902, **81**, 284) as the result of the interaction of commercial xylylene and methylene di-iodide. When, however, a higher temperature is employed, the tube being heated at once to 270–290°, no diamine can be detected, but, instead, a small yield of 1:3:7:9-tetramethylacridine is obtained. The mesophenyl derivative of this base was prepared by Ullmann and Weintraub from the *p*-line by the action of benzaldehyde (*Ber.*, 1903, **36**, 1021).

*1:3:7:9-Tetramethyldimethylenediamine*,  $\text{C}_6\text{H}_2(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$  (Senior and Goodwin).

The semicrystalline contents of the tube were heated with methylated spirit containing a small proportion of potassium hydroxide, and the solution obtained was allowed to cool, when small, yellow needles appeared, which were collected and washed successively with water and methylated spirit, and finally recrystallised from the latter solvent several times. The base consists of almost colourless needles, which melt at 128° (corr.). On analysis:

0.553 gave 21.6 c.c. moist nitrogen at 14.2° and 754 mm. N = 11.48.  
 $\text{C}_{17}\text{H}_{22}\text{N}_2$  requires N = 11.92 per cent.



The tube containing the xylylene and methylene dichloride was heated to 270–290° and kept at that temperature one and a-half to



two hours. Toward the close of the heating, a yellow sublimate was slowly collected at the cooler end of the tube. The contents were treated with cold ethyl acetate or acetone, and the dark brown powder remaining was dissolved in hot dilute hydrochloric acid, which solution on cooling deposited golden brown needles. The crystals were collected, treated with concentrated ammonium hydroxide solution, and washed with water. The base thus obtained, consisting of a white powder, was dissolved in hot methylated spirit, which on cooling yielded a pale yellow, silky needles. After several recrystallisations, crystals were obtained which melted constantly at  $122^{\circ}$  (corr.).  $1:3:7$  *tetranitrobenzidine* is also very soluble in cold ether or chloroform, less so in cold acetone, benzene, or pyridine. Its solution in methylated spirit shows faint blue fluorescence. On analysis:

0.1532 gave 0.1871  $\text{CO}_2$  and 0.1016  $\text{H}_2\text{O}$ . C = 86.71; H = 7.37.

0.1915 " " 98 c.c. moist nitrogen at  $14.5^{\circ}$  and 752 mm. N = 5.1.

$\text{C}_{12}\text{H}_{12}\text{N}_4$  requires C = 86.81; H = 7.23; N = 5.96 per cent.

*Platinichloride*,  $\left[ \text{C}_6\text{H}_5\text{Me}_2 \underset{\text{C}_{11}}{\overset{\text{N}}{\text{C}}} > \text{C}_6\text{H}_5\text{Me}_2 \right]_2, \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ .

brown crystals of this compound were obtained by adding a few drops of concentrated platinum chloride solution to a solution of the base in methylated spirit. The crystals were washed with ether and dried at  $105^{\circ}$ . The compound crystallises readily from a mixture of equal volumes of glacial acetic and concentrated hydrochloric acids. On analysis:

0.0418 gave 0.0092 Pt. Pt = 22.01.

$\text{C}_{24}\text{H}_{26}\text{N}_2\text{Cl}_6\text{Pt}$  requires Pt = 22.14 per cent.

*Aurichloride*,  $\text{C}_6\text{H}_5\text{Me}_2 \underset{\text{C}_{11}}{\overset{\text{N}}{\text{C}}} > \text{C}_6\text{H}_5\text{Me}_2, \text{HAuCl}_4$ .—A few drops of

solution of gold chloride were added to a solution of the base in mixture of concentrated hydrochloric and glacial acetic acids, when yellow precipitate separated. This was collected, washed with ether, and dried at  $195^{\circ}$ . On analysis:

0.6528 gave 0.0180 Au. Au = 34.09.

$\text{C}_{12}\text{H}_{11}\text{NCl}_4\text{Au}$  requires Au = 34.28 per cent.

*Picric acid*,  $\text{C}_6\text{H}_5\text{Me}_2 \underset{\text{C}_{11}}{\overset{\text{N}}{\text{C}}} > \text{C}_6\text{H}_5\text{Me}_2, \text{C}_6\text{H}_3(\text{NO}_2)_3 \cdot \text{OH}$ .—This salt was

obtained by adding a hot solution of picric acid in methylated spirit to hot solution of the base in the same solvent. Yellowish-brown, glistening crystals separated on cooling, which were collected, washed with methylated spirit, recrystallised from benzene, and dried at  $119^{\circ}$ . It melted at  $210-214$  (uncorr.). On analysis:

0.1699 gave 17.1 c.c. moist nitrogen at 16 and 758 mm. N = 11.7.

$\text{C}_{23}\text{H}_{20}\text{O}_7\text{N}_4$  requires N = 12.07 per cent.

*Condensation of a Mixture of m-4-Xylidine and m-4-Xylenol with Methylene Dichloride: 1:3:7:9-Tetramethylacridine.*

1:3:7:9-Tetramethylacridine is readily obtained by this method, and the yield is better than by that just described. m-4-Xylidine (1 mol.), m-4-xylenol (1 mol.), and methylene dichloride (1 mol.) were heated in a closed tube at 270—290° for two hours. The contents of the tube were treated with cold acetone or ethyl acetate and the insoluble portion was crystallised from dilute hydrochloric acid, the resulting hydrochloride decomposed with ammonium hydroxide, and the base recrystallised twice from methylated spirit. Some ammonium hydroxide was added to the solution in methylated spirit before the final recrystallisation, but not enough to cause a turbidity, in order to ensure complete decomposition of the salt. The crystals were finally washed with water and crystallised again from dilute spirit. They melted as before at 122° (corr.). On analysis:

0.804 g. gave 0.2555 CO<sub>2</sub> and 0.0535 H<sub>2</sub>O. C = 86.67; H = 7.39.

0.490 „ „ 5.2 c.c. moist nitrogen at 16.5° and 756 mm. N = 5.78.

C<sub>16</sub>H<sub>14</sub>N requires C = 86.81; H = 7.23; N = 5.96 per cent.

*Condensation of a Mixture of m-4-Xylidine and m-4-Xylenol with Methylene Diiodide: 1:3:7:9-Tetramethylacridine.*

An experiment was made with m-4-xylidine, xylenol, and methylene diiodide, which, on account of the high boiling point of the diiodide, could be performed in an open vessel. The dark brown liquid which resulted was treated in a similar manner to that described above for the contents of the closed tubes. The crystals obtained had the same melting point, and were identical in appearance with 1:3:7:9-tetramethylacridine.

*Condensation of p-Xylidine with Methylene Dichloride.*

With p-xylidine, the corresponding methylenedianiline was obtained readily, but, although repeated attempts were made even at temperatures 100° and upwards, we did not succeed in isolating the corresponding tetramethylacridine. The base was obtained, however, by other methods.

*1:4:5-Dimethylmethylenedianiline, C<sub>12</sub>(NH·C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>)<sub>2</sub>.*

p-Xylidine (2 mols.) and methylene dichloride (rather more than 2 mols.) were heated in a closed tube for two and a half hours at

170°–175°. The contents of the tube were dissolved in hot methyl spirit, and the solution was precipitated by a solution of potassium hydroxide. The precipitate was washed with water, dried, and reprecipitated twice from light petroleum. The base consists of brown needles, which soften at 135° and melt at 138°. It is soluble in chloroform, benzene, light petroleum, alcohol, or glacial acetic acid, but less so in ether. On analysis:

0.00114 gave 0.3475  $\text{CO}_2$  and 0.2447  $\text{H}_2\text{O}$ .  $\text{C} = 80.35$ ;  $\text{H} = 8.7$ .

0.2456 " " 23.4 c.c. moist nitrogen at 17° and 756 mm.  $\text{N} = 11.02$ .

$\text{C}_6\text{H}_8\text{N}_2$  requires  $\text{C} = 80.31$ ;  $\text{H} = 8.66$ ;  $\text{N} = 11.02$  per cent.

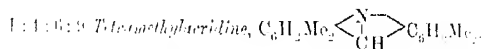
*Platinichloride*,  $(\text{CH}_3\text{NH}(\text{C}_6\text{H}_4\text{Me}_2))_2\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ .—A soluble platinide chloride was added to a solution of the base in methyl spirit containing a small proportion of hydrochloric acid. The crystalline precipitate obtained was washed with ether and dried at 140°. On analysis:

0.1063 gave 0.06363 Pt.  $\text{Pt} = 28.50$ .

$\text{C}_6\text{H}_8\text{ON}_2\text{Cl}_2\text{Pt}$  requires  $\text{Pt} = 28.57$  per cent.

### 5. *Condensation of a Mixture of p-Xyldine and p-Xylenol with Methylene Dichloride.*

When p-xyldine and xylenol are gradually heated in a closed tube with methylene dichloride to 250°–270°, the xylenol takes no part in the reaction and 1:1:5 dixylyl-methylenediamine, described above, is formed. The diamine was identified by its melting point, solubility, and appearance. A different result is obtained if the mixture is heated rapidly to about 300° or upwards, when acridine condenses in the highest amount.



p-Xyldine (1 mol.), p-xylenol (1 mol.), and methylene dichloride (3 mol.) were heated in a closed tube rapidly to 270° and this temperature was gradually increased to about 350°. The heating lasted from two to two and a half hours, the temperature being maintained for nearly an hour. The contents of the tube did not be separated by means of acetone, as was the case of the isomeride above described. They were dissolved in warmed filtered spirit, giving a solution with reddish-green base. This solution was precipitated by a concentrated solution of potassium hydroxide, and the resulting pale brown powder was collected, washed, and then distilled under reduced pressure. A yellow, crystalline sublimate was obtained, which, after being recrystallised twice from methylated spirit and finally from ethyl acetate, consisted of green

crystals which melted at 179.5–180.5° (corr.). The base is slightly soluble in ether, chloroform, or benzene, less so in acetone, carbon tetrachloride, or light petroleum. The pure base dissolved in methylated spirit exhibits a pale blue fluorescence. On analysis:

0.100 g. gave 0.6110 CO<sub>2</sub> and 0.1314 H<sub>2</sub>O. C = 86.52; H = 7.58.

0.100 g. gave 9.4 c.c. moist nitrogen at 15.5° and 774 mm. N = 5.57.

C<sub>17</sub>H<sub>13</sub>N requires C = 86.81; H = 7.23; N = 5.96 per cent.

(2) *Aurichloride*, C<sub>17</sub>H<sub>12</sub>Me<sub>2</sub>< $\begin{smallmatrix} \text{N} \\ \text{CH} \end{smallmatrix}\text{N}\text{AuCl}_4$ >C<sub>17</sub>H<sub>12</sub>Me<sub>2</sub>.HAuCl<sub>4</sub>.—A few drops of concentrated gold chloride were added to a solution of the base in methylated spirit with which a small proportion of hydrochloric acid had been mixed. An orange precipitate formed immediately, which was collected with methylated spirit and dried at 105°. On analysis:

0.100 g. gave 0.0247 Au. Au = 34.21.

C<sub>17</sub>H<sub>13</sub>NCl<sub>4</sub>Au requires Au = 34.28 per cent.

*Condensation of Dicyllylmethylenediamines with Xylidines and Xylidine Hydrochlorides: 1:3:7:9- and 1:4:6:9-Tetramethylacridines*

(1) Dicyllylmethylenediamine (1 mol.), *m*-1 xylidine (1 mol.), and its hydrochloride (1 mol.) were heated in a closed tube for two hours at 270–300°. The semi-solid, green mass in the tube was dissolved with cold acetone and the green, fluorescent solution was separated by pouring it into water. A yellow precipitate was formed, which was boiled for a few minutes with a solution of sodium hydroxide in methylated spirit, washed with water, and repeatedly distilled several times from methylated spirit. The resulting base was found to be identical in melting point, solubility, and crystalline appearance with 1:3:7:9-tetramethylacridine. The *aurichloride* was prepared, and on analysis:

0.100 g. gave 0.0235 Au. Au = 34.45.

C<sub>17</sub>H<sub>13</sub>NCl<sub>4</sub>Au requires Au = 34.28 per cent.

(2) 1,5-Dicyllylmethylenediamine, heated in a similar manner to (1) with *p*-xylidine and its hydrochloride, gave a black mass, which was dissolved in methylated spirit, the solution precipitated by addition of potassium hydroxide, collected, dried, and distilled under reduced pressure. The semicrystalline distillate was washed with water and recrystallised from methylated spirit containing a little sodium hydroxide. From its melting point, solubility, appearance, and behaviour when distilled, the base was identified as 1:4:6:9-tetramethylacridine. The *aurichloride* was prepared, and on analysis:

0.100 g. gave 0.0218 Au. Au = 34.22.

C<sub>17</sub>H<sub>13</sub>NCl<sub>4</sub>Au requires Au = 34.28 per cent.

7. *Condensation of  $\epsilon$ -Cumidine with Methylene Dichloride*  
 1:3:4:6:7:9-Hexamethylacridine (Senier and Goodwin)

$\epsilon$ -Cumidine (2 mols.) and methylene dichloride (1 mol.) were placed in a thick glass tube at 210–240° for three hours. The contents of the tube were washed by adding a mixture of methylated spirit and a solution of potassium hydroxide, heating the whole to boiling, then setting aside to cool. The insoluble residue was then washed carefully with cold acetone, the harder portions being rubbed in a mortar with the solvent. After this treatment, a few crystalline plates from ethyl acetate, benzene, or glacial acetic acid gave the base of high purity, melting at 217° (222° corr.), the same as found by Senier and Goodwin. On analysis:

0.2461 gave 0.7811  $\text{CO}_2$  and 0.1752  $\text{H}_2\text{O}$ . C = 86.49; H = 7.98;  
 $\text{C}_{24}\text{H}_{18}\text{N}_2$  requires C = 86.69; H = 7.98 per cent.

8. *Condensation of  $\psi$ -Cumidine and Methylene Dichloride*  
 1:3:4:6:7:9-Hexamethylacridine (Senier and Goodwin)

Mr. P. C. Austin, in the course of experiments in which he frequently to prepare hexamethylacridine, discovered some modifications of the original method for its preparation, and was under certain conditions he noticed the formation of an intermediate compound which is probably di- $\psi$ -cumylmethylenediamine.

Mr. Austin finds that alkali, either as carbonate or hydroxide, is essential in the preparation of the base, and that, if small quantities are desired, the operation can be conducted in a few minutes over an open flame in a test tube without any danger of over-heating. 12 grams of  $\psi$ -cumidine are melted, a few drops of methylene dichloride added, and the mixture warmed until the reaction begins. As soon as the first violence has subsided, the remainder of the methylene dichloride is added, and the liquid is boiled for one or two minutes. After cooling, the mass is heated to boiling with a solution of potassium hydroxide in methylated spirit, and from the clear solution, on cooling, greenish-yellow crystals of hexamethylacridine are obtained at once.

The colorless compound, di- $\psi$ -cumylmethylenediamine, was obtained, for example, in the following experiment.  $\psi$ -Cumidine (12 gram), methylene diiodide (9 grams), and potassium hydroxide (10 gram) were heated together to 190° in an oil-bath, using a reflux condenser. As soon as the reaction began, the flask was cooled for a few minutes after which, when it became more moderate, the heating was resumed and continued for several hours. After cooling, the contents of the flask were boiled with water to remove the alkali, the residue was then washed with water and with a little cold acetone, and finally extracted

with acetone. From the clear solution, colourless crystals were obtained on standing. They are very soluble in ether, carbon tetrachloride, chloroform, acetone, ethyl acetate, benzene, or glacial acetic acid, but less so in alcohol. The solutions exhibit no fluorescence. This compound is probably *di- $\alpha$ -cumylmethylenecrimine*,  $\text{N}(\text{H} \cdot \text{C}_6\text{H}_4\text{Me})_2$ . A *platinichloride* was prepared. On analysis: 0.2035 g. gave 0.0336 Pt. Pt = 27.25.

$\text{C}_{23}\text{H}_{23}\text{N}_2\text{Cl}_6\text{Pt} \cdot \text{H}_2\text{O}$  requires Pt = 27.46 per cent.

This compound was at first thought to be a hydro-derivative of hexamethylacridine, especially as by treatment with bromine in a carbon tetrachloride solution hexamethylacridine was formed, but no hydro-derivative of the latter could be obtained by reduction. The compound will be further examined, but meanwhile it may be noted that *platinichloride*, which forms gradually, is nearly colourless, its *platinichloride* is yellow, its solutions are not fluorescent, and it is easily soluble in either ethyl acetate or acetone; whilst hexamethylacridine *platinichloride* is red and forms immediately, its *platinichloride* is red, its solutions are fluorescent, and it is not easily soluble in ethyl acetate or acetone.

*Condensation of m-4-Xylydine and  $\alpha$ -Naphthol with Methylene Dichloride:* 9:11-Dimethylphenyl- $\text{N}^{\alpha}$ - $\alpha$ -naphthylacridine,  $\text{C}_{26}\text{H}_{26}\text{Me}_2 \left\langle \begin{smallmatrix} \text{N} \\ \text{CH} \end{smallmatrix} \right\rangle \text{C}_{10}\text{H}_6$ .

*m*-4-Xylydine (1 mol.),  $\alpha$ -naphthol (1 mol.), and methylene dichloride (10 vols.) were heated for two hours in a closed tube at 250–260°. The thick, viscous mass, after cooling, was first well washed with ether. The deep yellow residue was then boiled for a few minutes in methylated spirit to which a small proportion of a solution of sodium hydroxide had been added, and the mixture was set aside to settle. The residue which remained was washed with water and also with methylated spirit, and then dissolved in amyl alcohol, from which it was crystallised several times. Light petroleum or glacial acetic acid were also used in some experiments as media for recrystallisation. The base forms small, yellow, glistening crystals which melt at 155–156° (corr.). It is very soluble also in benzene, toluene, or chloroform. In solution in amyl alcohol, it shows a blue, and in glacial acetic acid a green, fluorescence. On analysis:

0.2556 g. gave 0.5377  $\text{CO}_2$  and 0.0910  $\text{H}_2\text{O}$ . C = 88.55; H = 6.10.

0.1713 g. gave 8 c.c. moist nitrogen at 13° and 756 mm. N = 5.49.

$\text{C}_{26}\text{H}_{26}\text{N}$  requires C = 88.71; H = 5.81; N = 5.45 per cent.

*Platinichloride*,  $\left[ \text{C}_{26}\text{H}_{26}\text{Me}_2 \left\langle \begin{smallmatrix} \text{N} \\ \text{CH} \end{smallmatrix} \right\rangle \text{C}_{10}\text{H}_6 \right]_2 \cdot \text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ . — A few

drops of a concentrated solution of platinum chloride were added to the base in a mixture of concentrated hydrochloric and phosphoric acids. The yellow precipitate which formed was washed with petroleum and dried at 110°. On analysis:

0.6020 gave 0.0610 Pt. Pt = 20.72.

$C_{17}H_{15}ON_2Cl_2Pt$  requires Pt = 20.70 per cent.

10. *Condensation of m-4-Xyldine and  $\alpha$ -Naphthol*

*Methylene Dichloride*: 9:11-Dimethylpheno- $\overset{N^a}{\underset{CH_3}{\text{C}_6\text{H}_3}}$ -acridine.

The xyldine, naphthol, and methylene di-iodide were heated in molar proportions. The xyldine and naphthol were heated in an open vessel and the methylene di-iodide was added in portions at a time. The heating was continued until the vigorous reaction was completed, and the resulting mass was purified in the manner just described (9). By their melting points, solubility, and appearance, the crystals obtained were identical with 9:11-dimethylpheno- $\overset{N^a}{\underset{CH_3}{\text{C}_6\text{H}_3}}$ -naphthaeridine.

11. *Condensation of m-4-Xyldine and  $\beta$ -Naphthol*

*Methylene Dichloride*: 9:11-Dimethylpheno- $\overset{N^{\beta}}{\underset{CH_3}{\text{C}_6\text{H}_3}}$ -acridine (Ullmann).

1 Xyldine (1 mol.),  $\beta$ -naphthol (1 mol.), and methylene di-iodide (1 mol.) were heated in a closed tube and the contents treated in the preparation of the  $\alpha$ -isomeride (9), except that, instead of being from amyl alcohol, the product, which was pale yellow, was dissolved in methylated spirit, precipitated therefrom with anhydrous hydroxide, and the precipitate washed with water and recrystallized from methylated spirit. The final crystallisation may also be effected from amyl alcohol. In solution in methylated spirit, the base exhibits a blue fluorescence. It melts at 153° (corr.), and is identical with that described by Ullmann (*loc. cit.*). On analysis:

0.61578 gave 0.5135  $CO_2$  and 0.0850  $H_2O$ . C = 88.74; H = 5.84.

$C_{17}H_{15}N_2$  requires C = 88.71; H = 5.84 per cent.

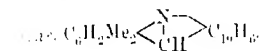
12. *Condensation of m-4-Xyldine and  $\beta$ -Naphthol*

*Methylene Dichloride*: 9:11-Dimethylpheno- $\overset{N^{\beta}}{\underset{CH_3}{\text{C}_6\text{H}_3}}$ -acridine (Ullmann).

Substituting methylene di-iodide in the experiment just described

fluoride, the same base is obtained. The operation is conducted at 100° in an open vessel.

*Reaction of p-Xylylene and  $\alpha$ -Naphthol with Methylene Dichloride: 8:11-Dimethylphenyl-N <sup>$\alpha$</sup> -naphthyl-  
acridine,  $C_6H_2Me_2 \langle \begin{smallmatrix} N \\ CH \end{smallmatrix} \rangle C_{10}H_7$*



One mole of p-xylylene (1 mol.),  $\alpha$ -naphthol (1 mol.), and methylene dichloride were heated in a closed tube to the same degree as in the preceding experiment with *m*-xylidine (9). The contents of the tube were treated also in the same manner, and the recrystallisation was carried out from amyl alcohol with final washing with methylated

spirit. The product consists of dull green needles which melt at 122.5°. It is soluble in acetone, benzene, or glacial acetic acid, less soluble in ethylated spirit, light petroleum, or amyl alcohol. Its solution in ethylated spirit shows blue fluorescence. On analysis:

0.2 g. gave 0.4583 CO<sub>2</sub> and 0.0764 H<sub>2</sub>O. C = 88.65; H = 6.02.

0.2 g. gave 6.6 c.c. moist nitrogen at 16.8° and 756 mm. N = 5.41.

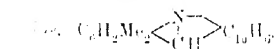
0.2 g. H<sub>2</sub>N requires C = 88.71; H = 5.81; N = 5.45 per cent.

*Platinum chloride*,  $\left[ C_6H_2Me_2 \langle \begin{smallmatrix} N \\ CH \end{smallmatrix} \rangle C_{10}H_7 \right]_2PtCl_6 \cdot 4H_2O$ . — To the solution of the base in glacial acetic acid, containing a small proportion of hydrochloric acid, a few drops of a concentrated solution of platinum chloride were added. The salt separated on standing as a precipitate, which was washed with glacial acetic acid, then with light petroleum, and dried at 100°. On analysis:

0.2 g. gave 0.0063 Pt. Pt = 20.86.

$C_{18}H_{24}ON_2Cl_6Pt$  requires Pt = 20.70 per cent.

*Reaction of p-Xylylene and  $\beta$ -Naphthol with Methylene Dichloride: 8:11-Dimethylphenyl-N <sup>$\beta$</sup> -naphthyl-  
acridine,  $C_6H_2Me_2 \langle \begin{smallmatrix} N \\ CH \end{smallmatrix} \rangle C_{10}H_7$*



The same base was obtained, using equal molecular proportions of p-xylylene,  $\beta$ -naphthol, and methylene dichloride, in the same manner

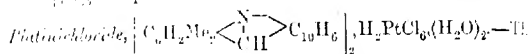


in the preparation of the  $\alpha$ -isomeride (13) just described, and that the final recrystallisations were effected from methylated benzene. It consists of small, well-formed, pale yellow, glistening needles, melting at 154° (correct). It is very soluble in benzene, toluene, petroleum, or glacial acetic acid. Its solution in methylated benzene exhibits faint blue fluorescence. On analysis:

0.1570 gave 0.5099  $\text{CO}_2$  and 0.0872  $\text{H}_2\text{O}$ .  $\text{C} = 88.57$ ;  $\text{H} = 6.17$ .

0.1296 " 0.8 cc. moist nitrogen at 17° and 764 mm.  $\text{N} = 5.5$ .

$\text{C}_{11}\text{H}_{12}\text{N}$  requires  $\text{C} = 88.71$ ;  $\text{H} = 5.84$ ;  $\text{N} = 5.45$  per cent.



was dissolved in a mixture of glacial acetic and concentrated sulphuric acids, and to this platonic chloride solution was added a yellow precipitate, which formed at once, was washed with light petroleum and dried at 115°. On analysis:

0.1284 gave 0.0261 Pt.  $\text{Pt} = 20.32$ .

$\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$  requires  $\text{Pt} = 20.31$  per cent.

#### 15. Condensation of $p$ -Nylidine and $\beta$ -Naphthol with *Meta*-Indole.

*Indole*: 8:11-Dimethyl- $\frac{\text{N}-\beta}{\text{CH}_a}$ -naphthacridine.

The same base was obtained by heating together as in the case of 12, in an open vessel,  $\beta$ -naphthol and methylene di-iodide.

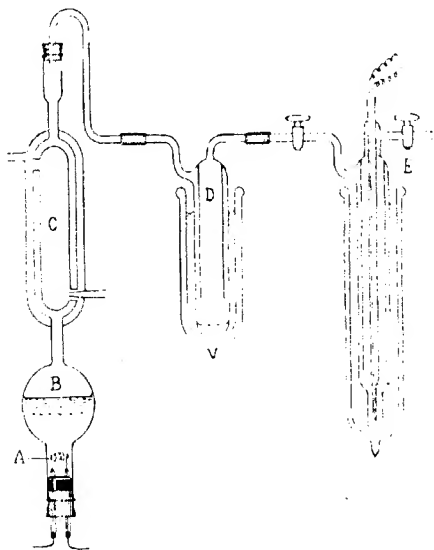
QUEEN'S COLLEGE,  
GALWAY.

### CLXXXVIII.—Keten.

By NORMAN THOMAS MORTIMER WILSMORE.

SOME time ago, Dr. A. W. Stewart and I attempted to prepare a set of compounds which we thought, might have a transitory existence during the course of certain isomeric changes. To this end, original substances were subjected to the action of a strongly reducing, somewhat in the way described by Löb (*Zeitsch. Elektrochem.* 1904, **10**, 504). The method was modified, however, in that the was kept below the surface of the liquid or solution, instead of being placed in the vapour space above it, as we believed that, by means, any initial products of the reaction would be more easily swept away from the hot zone before they could be further decomposed.

course of the work, we were led to try the action of the hot wire on a variety of substances. Most of the results obtained have no place on the present paper; but, in the case of ethyl acetate, propyl acetate, and especially of acetic anhydride, we found that the gases evolved contained a substance which had a peculiar pungent smell, which could be condensed to a liquid in a bath of solid carbon dioxide and acetone. We gave a preliminary description of this substance in a letter to *Nature* (1907, 75, 510), and we suggested that it might be the lowest member of the keten series. Since then, my work has been unfortunately prevented from taking an active



part in the work. In the present communication, I propose to offer some evidence in support of the above suggestion.

The apparatus used for the isolation of the new substance is shown in the accompanying figure. *A* is the heating coil of thin wire. For this platinum has been used for this, but probably other fairly fusible metals would serve as well. This wire must be replaced frequently, as it quickly becomes covered with a hard, elastic film which greatly reduces its activity. An arc, burning between two metallic electrodes, may be substituted for the heating coil; but it requires more attention, and, so far, the results have not been

Fig. 1. The heating coil is attached to leads of stout platinum, sealed into glass tubes, which pass through the rubber stopper in *A*. A layer of mercury protects the rubber stopper from contact with the liquid contained in the vessel *B*. The latter is connected directly to the chloride surface reflux condenser, *C*. The trap, which is cooled by means of solid carbon dioxide and acetone, is intended to catch any spray or vapour of the original liquid in *B* which may escape from *C*. The vessel, *E*, in which the substance is to be condensed, is immersed in a cooling-bath, kept at about  $-100^{\circ}$  by the addition of liquid air. The tube in the centre of *E* is closed at the lower end, and contains a thermo-junction for measuring the temperature. To fractionate any liquid which has condensed in the latter is first cooled in a bath of liquid air. This bath is then replaced by a glass jacket, covered, except at its closed lower end, with some insulating material, and the whole is placed on a block of metal, which, by conducting heat to the bottom of *E*, produces the effect of a small, mild flame in an ordinary distillation. A platinum "tetrahedron" facilitates ebullition.

I have not yet succeeded in obtaining the new compound in a pure state. Carbon dioxide, acetylene, and other hydrocarbons always liquified along with it, and cannot be easily separated (fractional distillation); also, its tendency to condense on standing at ordinary temperature and its great reactivity increase the difficulty of manipulation. Nevertheless, four analyses gave as a mean result, on exploding 1 volume of the gas with excess of dry oxygen, there was a contraction of 1.09 volumes, whilst the residue contained 1.57 volumes of carbon dioxide, and 2.08 volumes of oxygen had disappeared. The corresponding numbers for a gas having the composition  $C_2H_2O$  should be 1:1:2:2. Also, three determinations of the density, by direct weighing in a bulb of about 160 c.c. capacity, gave 1.174 as a mean value for the molecular weight, instead of 12.

As far as they have yet been studied, the reactions of the substance correspond with those of the ketens as described by Staudinger (*Ber.* 1906, **38**, 1735; 1906, **39**, 968, 3062; 1907, **40**, 1145; *Ann.* 1907, 356, 514). Thus, in general, it behaves as an internal anhydride of acetic acid. With ethyl and amyl alcohols, it gave the corresponding ester, recognised by their smell, and by their giving a ferric chloride reaction for acetates after saponification. Also, in the case of the ethyl ester, a sample was obtained which, after distillation from phosphorus pentoxide, boiled at  $76^{\circ}$ . Primary amines absorbed the gas rapidly at the ordinary temperature. With aniline, acetanilide was formed, which, after recrystallisation from benzene, or even after evaporating off the excess of aniline on a watch-glass in the air, melted sharply at  $112^{\circ}$ . The melting point was not altered by the

the acetanilide made in the usual way. Similarly, from *o*-toluene and *o*-toluidide, melting at  $110^{\circ}$ , was produced, and, from liquid ammonia, acetamide, melting at  $79^{\circ}$ . The substance reacts vigorously with bromine. On distilling off the excess of bromine and adding alcohol to the residue, there was a further evolution of heat, and the residue had the characteristic pungent smell of acetic ester, indicating that bromoacetyl bromide had first been formed.

It can therefore be no doubt that the new substance is a *keten*, of the formula  $\text{CH}_2\text{:CO}$ , although, as distinguished from Singer's disubstituted ketens, it may also exist in the form  $\text{H}_2\text{C=OH}$ .

All the above-mentioned reactions begin readily at the ordinary temperature, and are, in fact, accompanied by evolution of heat. *Keten* seems likely to prove a useful acetylating agent. It has a special advantage over other acetylating agents in that no by-products are formed in the reaction.

*Keten* has a peculiar penetrating smell, which persists for many hours if the gas has been inhaled in any but small quantities, and it irritates the mucous membranes. It is colourless in both the liquid and gaseous states, and on freezing it forms a white solid. It does not appear to react with dry oxygen, but it combines rapidly with water, yielding, for the most part, acetic acid. The aqueous solution, however, gives the chief reactions for an aldehyde, so that glycollaldehyde may be formed in small quantity at the same time. It may be noted that, if *keten* could be made to react with water in the isomeric form  $\text{CH}_2\text{CO}\cdot\text{H}$ , there would be a possibility of building up from it compounds containing the group  $\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot$ .

The tendency of *keten* to condense on standing to a brown liquid has been already referred to. In the gaseous state, at the ordinary temperature and pressure, the reaction is fairly slow, that is to say, it is possible, by working quickly, to obtain a fair measurement of the rate in a gas burette, and the rate is further diminished by dilution with an indifferent gas. But in the liquid state, under pressure, the reaction is rapid and much heat is evolved. Porous substances, such as charcoal, also hasten the reaction. The condensation product has not been studied.

The research is being continued.

UNIVERSITY COLLEGE,  
UNIVERSITY OF LONDON.



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# ERRATA.

## ERRATA.

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### PART I.

Page	Line	
505	23	for "1904, ii, 42" read "1904, i, 480."
508	17*	" "the" read "methyl."
508	17*	" "thul" read "αγ-dimethyl ββ-dithyl."
508	16*	" "C(CO <sub>2</sub> Et) <sub>3</sub> (C≡N)·CO <sub>2</sub> Et <sub>2</sub> " read "C(CO <sub>2</sub> Et) <sub>3</sub> CH(CN)·CO <sub>2</sub> Et."

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765		transpose Fig. 3 to page 767.
767		Fig. 2 " 763.
1591	2	for "7(10)-amino-1-naphthacenequinone" read "7(10)-amino-1-hydroxynaphthacenequinone"
1649	1*	" "C <sub>15</sub> H <sub>12</sub> O <sub>4</sub> " read "C <sub>15</sub> H <sub>12</sub> O <sub>4</sub> ."

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### PART I.

952	11	for "6-hydroxy-4-isopropylflavone" read "6-methoxy-4-isopropylflavone"
952	12	}
952	25	
952	1*	
953	16	
957	23	" "Dioxycodeine" read "Deoxycodeine."

\* From bottom.

acetanilide made in the usual way. Similarly, from *o*-toluenesulfonyl-toluidide, melting at  $110^{\circ}$ , was produced, and, from liquid ammonia, acetamide, melting at  $79^{\circ}$ . The substance reacts vigorously with bromine. On distilling off the excess of bromine and adding alcohol to the residue, there was a further evolution of heat, and the residue had the characteristic pungent smell of an ester, indicating that bromoacetyl bromide had first been

formed. There can therefore be no doubt that the new substance is a *keten*, with the formula  $\text{CH}_2\text{:CO}$ , although, as distinguished from other disubstituted ketens, it may also exist in the form of a dimer.

All the above-mentioned reactions begin readily at the ordinary temperature, and are, in fact, accompanied by evolution of heat. *Keten* seems likely to prove a useful acetylating agent. It has a decided advantage over other acetylating agents in that no by-products are formed in the reaction.

*Keten* has a peculiar penetrating smell, which persists for many minutes if the gas has been inhaled in any but small quantities, and it irritates the mucous membranes. It is colourless in both the liquid and gaseous states, and on freezing it forms a white solid. It does not appear to react with dry oxygen, but it combines rapidly with water, forming for the most part, acetic acid. The aqueous solution, however, carries the chief reactions for an aldehyde, so that glycollaldehyde is formed in small quantity at the same time. It may be noted that, if *keten* could be made to react with water in the isomeric form  $\text{CH}_2\text{CO}\cdot\text{H}$ , there would be a possibility of building up from it compounds containing the group  $\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot$ .

The tendency of *keten* to condense on standing to a brown liquid has already been referred to. In the gaseous state, at the ordinary temperature and pressure, the reaction is fairly slow, that is to say, it is possible, by working quickly, to obtain a fair measurement of the rate in a gas burette, and the rate is further diminished by dilution with an indifferent gas. But in the liquid state, under pressure, the reaction is rapid and much heat is evolved. Porous substances, such as asbestos, also hasten the reaction. The condensation product has not yet been studied.

Research is being continued.

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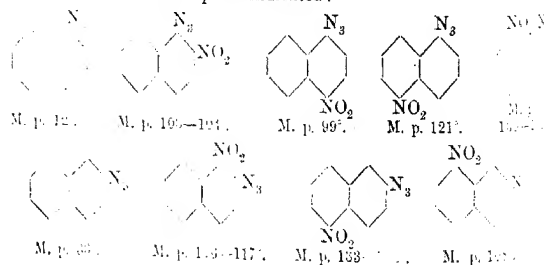


# CLXXXIX.—Aromatic Azoimides. Part III. 7 Naphthylazoimides and their Nitro-Derivatives

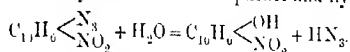
By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

THE failure of an attempt to explain the peculiar behaviour of phenylazoimide from a study of the hydroxyphenylazoimides (this J. 855 and 1359), led us to consider the possibilities of other triazopentols, and derivatives of partly hydrogenised naphthalene series themselves. There is, however, no available information respecting azoimides of naphthalene itself, and the present communication is with this matter, as preliminary to the investigation of the compounds which might be expected to bear more directly on the original problem.

The principal interest with which previous work has investigated aromatic azoimides lies in the influence exerted on the properties of the triazo-group by neighbouring substituents. Many examples of this correlation might be quoted, such as the elimination of hydrazoic acid from *p*-nitrophenylazoimide by alcoholic potash, the removal of nitrogen from benzylazoimide by acids, and the colour change undergone by the potassium derivative of *p*-hydroxyphenylazoimide. In dealing with substituted azoimides of the naphthalene series, it was in the first place desirable to ascertain the relationship between the nitro- and triazo-groups with respect to the possibility of eliminating the latter with alcoholic potash. Noelting, Grandmougin, and Mitz (Ber., 1892, 25, 3328) investigated this point in connexion with the nitrophenylazoimides, and have shown that the nitro-group is without influence in the meta-position, the change in question occurring also with ortho- and para-derivatives. We find that whilst the  $\alpha$ - and  $\beta$ -naphthylazoimides resist the action of alcoholic potash, and the homonuclear nitro-groups in the favourable positions encourage elimination of hydrazoic acid, heteronuclear substitution appears to be inefficient. The following compounds have been prepared and examined from the standpoint indicated:

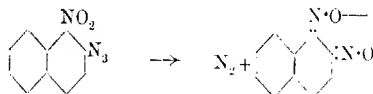


The only members of this series which yield hydrazoic acid under the influence of alcoholic potash are 2-nitro-1-naphthylazoimide, 4-nitro-1-naphthylazoimide, and 1-nitro-2-naphthylazoimide; of these, the ortho-compound yields about 50 per cent. of the hydrazoic acid required by theory as compared with 30 per cent. obtainable from *o*-nitrophenylazoimide, whilst the para-compound, 4-nitro-1-naphthylazoimide, is converted quantitatively into 4-nitro-1-naphthol and hydrazoic acid:



The smoothness of this reaction compares favourably with the corresponding change undergone by *p*-nitrophenylazoimide, which yields only 10 per cent. of the hydrazoic acid required by theory (Noelting, Erdmington, and Michel, *loc. cit.*), whilst *p*-nitrophenol could not be obtained in the product, having undergone ethylation and reduction to *p*-ethoxyphenetole.

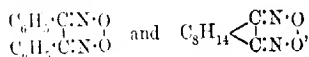
It was to be expected that, hydrazoic acid being obtainable from 2-nitro-1-naphthylazoimide, the closely related ortho-derivative of the series, namely, 1-nitro-2-naphthylazoimide, would also part with its azo-group. But although 30 per cent. can be obtained under favourable conditions, the reaction is complicated by a remarkable change which takes place slowly when the dissolved substance is aged alone in alcohol, involving loss of nitrogen in two atomic proportions; in glacial acetic acid at 110°, the alteration proceeds quantitatively, and there arises the peroxide of  $\beta$ -naphthoquinone-oxime:



Noelting and his collaborators refer to the fact that *o*-nitrophenylazoimide (m. p. 51—52°) decomposes at 75—80°, yielding a volatile compound melting at 65—67° (*loc. cit.*, p. 3339), whilst Zincke (*J. pr. Chem.*, 1896, [ii], 53, 340; compare also Drost, *Annalen*, 1899, 307, 103) investigating several typical *o*-nitro-derivatives of phenylazoimide, has shown that all such compounds lose two nitrogen atoms, furnish products which he describes as ortho-dinitroso-compounds. We are to think that this view of their constitution is misleading, and take the opportunity of drawing attention to the matter, because considerable number of such compounds have been prepared by these workers, and catalogued in the literature as dinitroso-derivatives, when really they should have been indexed as quinone-oxime peroxides. The following is a list of such derivatives: 1,2-Dinitrosonaphthalene (Koreff, *Ber.*, 1886, 19, 182, and von Doeh, *Ber.*, 1886, 19, 349).

- p*-Dinitrosobenzene (Nietzki and Kehrman, *Ber.*, 1887, **20**, 615).  
 1:4-Dinitro-*o*-naphthalene (Nietzki and Guitermann, *Ber.*, 1888, **21**, 131).  
 2:5-Dinitrosotoluene (Nietzki and Guitermann, *loc. cit.*, and *Monatsh. Ber.*, 1888, **21**, 734).  
 2:5-Dinitro-*p*-xylene (Pülig, *Annalen*, 1889, **255**, 176).  
*o*-Dinitrosobenzene (Zincke and Schwarz, *Annalen*, 1899, **307**, 1).  
 2:3- and 3:4-Dinitrosotoluenes (Zincke and Schwarz, *loc. cit.*).  
 1:5-Dinitro-*o*-*m* xylene (Zincke and Schwarz, *loc. cit.*).  
*p*-Dinitrosouisoide (Best, *Annalen*, 1889, **255**, 187).  
*p*-Dinitrosocymene (Kehrman and Messinger, *Ber.*, 1890, **23**, 3560).  
 Nitro-derivatives of *o*-dinitrosobenzene (Drost, *Annalen*, 1899, **307**, 46).  
 1:2:3:4-Tetranitrosobenzene (Nietzki and Geese, *Ber.*, 1890, **23**, 505).

The above compounds were prepared from the corresponding dioxime by oxidation, generally in alkaline solution with potassium ferricyanide; some of them have been shown to yield the original dioxime when carefully reduced, and in no case do the physical properties suggest the presence of a true nitroso-group. It is therefore unreasonable to regard them as analogous to the peroxides of benzodioxime and camphorquinonedioxime,



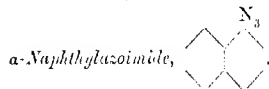
neither of which can possibly be classified as normal nitroso-compounds. None of the authors who describe the compounds enumerated appear to attach much importance to the alternative constitution, excepting Koreff (*Ber.*, 1886, **19**, 183); some among the other authors content themselves with mentioning the peroxido formula, while retaining the misleading name, and the remaining ones ignore it altogether. Moreover, Auwers and Meyer (*Ber.*, 1888, **21**, 804) and Scholl (*Ber.*, 1887, **20**, 3427) refer to the work of Koreff, without pointing out the likelihood of the derivatives described by him being genuine nitroso-compounds, whilst Bridge (*Annalen*, 1893, **277**, 79) states that the oxidation product obtained by Nietzki and Kehrman (*Ber.*, 1887, **20**, 615) from quinonedioxime must be regarded as *p*-dinitrosobenzene. As recently as 1903, the peroxides of *o*-benzophenonedioxime and of diquinoylketoxime are referred to erroneously as *o*-dinitrosobenzene and tetranitrosobenzene respectively (Jahres-Schmidt, "Die Nitrosoverbindungen"; Ahrens' *Vorträge*, Vol. VII).

On comparing the behaviour of 2-nitro-1-naphthylazoinide with that of 1-nitro-2-naphthylazoinide, it is found that the former substance

nitrogen much less readily, solutions in glacial acetic acid and benzene appearing to undergo no change when boiled; the solid material, however, begins to yield gas above the point of fusion, decomposition proceeding rapidly at about 150°. From this it is evident that the  $\alpha$ -position for the triazo-group is less favourable to change in question than the neighbouring one, and examination of other nitronaphthylazoimides indicates that only those in which the triazo group has assumed the ortho-position give rise to a definite point of decomposition. The facility with which the change occurred in the case of 1-nitro-2-naphthylazoimide encouraged us to suppose that it might be possible to obtain, through its dioxime peroxide, hitherto unknown 1:5-naphthaquinone, because these positions are synpathetic, and the recent work of Willstätter has established the existence of an amphi-naphthaquinone, namely, the 2:6-derivative (Willstätter and Parnas, *Ber.*, 1907, **40**, 1406). The attempt failed, however, and we were unsuccessful also in the case of the 1:8-derivative, but it is well known that a structural difficulty presents an obstacle to formulating the peri-naphthaquinone.

In this communication, we describe the azoimides from seven nitronaphthylamines. They are coloured various shades of brown and yellow, but darken rapidly when exposed to light; the substances crystallise with such readiness, and are prepared so easily from the respective naphthylamines, that they offer a means of identifying small quantities of these bases.

## EXPERIMENTAL.



In the first attempts to prepare this compound, we made use of the method which gave satisfactory results in the case of *p*-hydroxyphenylazoimide, namely, the action of hydroxylamine on the diazonium salt (H. Fischer, *Annalen*, 1877, **190**, 96); the discouraging yield, which amounted to less than 5 per cent., led us to try the action of hydrazine, but in this case also the proportion of azoimide obtained was trifling, the greater part of the material remaining after steam distillation in the form of a tough, black resin, which develops a beautiful greenish-brown coloration with concentrated sulphuric acid. No variation in the experimental conditions leading to improvement, we had recourse ultimately to the method described by Noelting and Michel (*Ber.*, 1896, **26**, 86), which consists in treating the diazonium salt with hydrochloric acid.

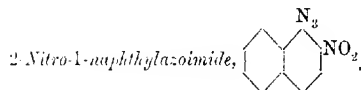
Thirty grams of  $\alpha$ -naphthylamine dissolved in 180 c.c. of glacial

acetic acid were mixed with 80 c.c. of concentrated sulphuric acid and diazotised with a solution of sodium nitrite containing 15 grams; after ten minutes, 5 grams of powdered carbamide were added to the ice-cold liquid, followed by 15 grams of sodium azide in 50 c.c. of water. A colourless turbidity was immediately developed, and torrents of nitrogen escaped. After several hours at zero, the oil was extracted with ether, the residue from which was then distilled in a current of steam, four hours being required to complete this process. The ethered solution of the distillate was pale brown, but lost its colour in two extractions with concentrated hydrochloric acid followed by 20 per cent. potash, and, when dried with calcium chloride, left on evaporation 27 grams of pale yellow, limpid oil, which crystallised in hard, lustrous prisms melting at  $12^{\circ}$ :

0.1993 gave 43.4 c.c. of nitrogen at  $21^{\circ}$  and 742 mm.  $N = 24.77$ .

$C_{11}H_7N_3$  requires  $N = 24.85$  per cent.

The substance has the persistent odour of ethoxynaphthalene; it is readily soluble in alcohol, and mixes in all proportions with ether and acetone. An attempt to distil under 2 mm. pressure was unsuccessful, decomposition taking place at about  $110^{\circ}$ . Like all the azonides described in this paper, it is decomposed with great vigour by concentrated sulphuric acid, torrents of nitrogen being evolved. Alcoholic potash failed to eliminate hydrazoic acid from  $\alpha$ -naphthylazonide, which was recovered unaltered after three days' treatment with the boiling agent. Nitration proceeded with unusual smoothness, 5 gram of the oil when mixed with 30 c.c. of nitric acid (sp. gr. 1.42) becoming solid in less than two minutes; the sole product was 4-nitro-1-naphthylazonide (see below).



The 2-nitro-1-naphthylamine required for preparing this azonide was made by the process of Lellmann and Remy (*Ber.*, 1886, 13: 802 and 893). Instead of nitrating the  $\alpha$ -acetonnaphthalide with nitric acid of sp. gr. 1.51, however, we used the corresponding quantity of the weaker agent, sp. gr. 1.42, and checked the tendency to substitution changes by adding carbamide. This is advantageous when 1:4:1-nitrobase is required, because the temperature may be raised to  $30^{\circ}$  or  $35^{\circ}$ , when it is found that 100 grams of  $\alpha$ -acetonnaphthalide yield only 30 grams of the molecular mixture of 4:1 and 2:1-nitro-compounds, instead of the 60 grams obtained at  $15^{\circ}$ ; the remainder in each case consisting of 4-nitro-1-acetonnaphthalide, which remains dissolved in the glacial acetic acid. The 2-nitro-1-az-

azole was hydrolysed with boiling dilute sulphuric acid and which furnishes a quantitative yield of the nitro-base in two steps is therefore more convenient than alcoholic potash, which gives a portion of the nitro-compound to 2-nitro-1-naphthol.

2-nitro-1-naphthylamine was diazotised in a mixture of glacial acetic acid and concentrated sulphuric acid, and, in presence of carbon dioxide, treated with hydrazoic acid; this led to immediate precipitation of the azoimide, which, when crystallised from dilute acetone, formed long, lustrous, yellow needles, melting at 103–104°, and decomposing very slowly at that temperature:

0.73 gave 24.6 c.c. of nitrogen at 21° and 760 mm.  $N = 26.22$ .

$C_{10}H_6O_2N_4$  requires  $N = 26.16$  per cent.

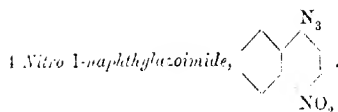
The compound is readily soluble in acetone, alcohol, or benzene, and petroleum dissolves it only sparingly.

*Decomposition by Heat.*—The behaviour of the 2-nitro-1-naphthylazoimide when heated is quite distinct from that of the isomeric 1-nitro-2-naphthylazoimide, although the product of the change is the same in each case. Solutions in glacial acetic acid, xylene, and nitrobenzene were boiled without yielding nitrogen, and the compound was recovered unchanged, although somewhat contaminated, from the last-named solvent. When heated alone, 2-nitro-1-naphthylazoimide begins to liberate gas very slowly above the melting point, effervescence becoming brisk towards 150°; the product was found to be identical with the  $\beta$ -naphthaquinonedioxime peroxide obtained from the isomeric 1-nitro-2-naphthylazoimide, crystallising from dilute alcohol in almost colourless needles melting at 127° without decomposition (von Ilinski, *Ber.*, 1886, **19**, 349; see also Koreff, *ibid.*, p. 176):

0.631 gave 34.4 c.c. of nitrogen at 22° and 756 mm.  $N = 15.15$ .

$C_{10}H_6O_2N_2$  requires  $N = 15.06$  per cent.

*Hydrolysis.*—Four grams of the azoimide were heated in alcohol with 10 c.c. of 5 per cent. potash during eight hours under reflux, red crystals of the potassium derivative of 2-nitro-1-naphthol appearing in the experiment; cold dilute sulphuric acid was added to the residue left by evaporation, and on distilling the filtrate, and neutralising the distillate, 0.6 gram of sodium azide was obtained, corresponding roughly to 50 per cent. of that required by theory. The 2-nitro-1-naphthol was recrystallised from alcohol, and melted at 128°.

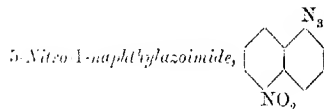


The *isimide* separated immediately on adding sodium azide to a solution of the diazonium salt from 4-nitro-1-naphthylamine. Recrystallised from boiling alcohol, it formed long, lustrous needles melting sharply at 99°.

0.0250 gave 21.5 c.c. of nitrogen at 20° and 757 mm.  $N = 26.1$  per cent.  
 $C_{10}H_6O_2N_4$  requires  $N = 26.16$  per cent.

The compound is identical with the product of nitrating 1-naphthylazoisimide; it dissolves very sparingly in cold methyl and ethyl alcohol, in benzene, and in hot petroleum. All attempts to convert the substance into *naphthoquinonedioxime* peroxide by eliminating nitrogen were unsuccessful.

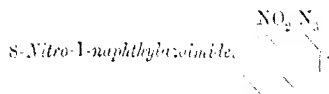
*Hydrolysis.*—Hot alcoholic potash resolved 5 grams into 2.5 g. of 4-nitro-1-naphthol (m. p. 164.5°) and 1.2 grams of sodium azide; the yield of the latter was therefore quantitative.



5-Nitro-1-naphthylamine, prepared by reducing 1:5-dinitro-naphthylamine with alcoholic ammonium sulphide and recrystallising the product from water, was diazotised and treated with hydrazine; the azoisimide appeared forthwith as a greenish-yellow precipitate and was recrystallised from boiling absolute alcohol, which deposits the substance in lustrous, yellow needles melting at 127°.

0.1213 gave 44.6 c.c. of nitrogen at 23° and 764 mm.  $N = 26.1$  per cent.  
 $C_{10}H_6O_2N_4$  requires 26.16 per cent.

Decomposition takes place rapidly at 130°, but the product is a solid in which it has not been possible to recognise the peroxide of 1:5-naphthoquinonedioxime. An attempt to hydrolyse the azoisimide with alcoholic potash converted the substance into a black powder which could not be identified; no trace of hydrazoic acid was recognisable, however.



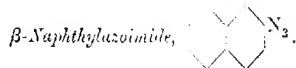
peri-nitronaphthylamine required for this preparation was made according to the directions of Meldola and Streatfield (*Trans.*, 1893, **1**, 27), based on those of Noetting and Collin (*Ber.*, 1884, **17**, 100). In the hope of improving the yield obtained by these chemists (10 per cent.), twelve experiments, each involving 200 grams of naphthylamine, were carried out under conditions varying in respect of temperature, and strength of acid from those laid down; we were unsuccessful, however, and found, furthermore, that the presence of water during nitration does not appear to influence the result in marked extent. On one occasion, 20 grams was obtained, but it was not possible to recognise the particular modification in the compound which led to this result, and we could not repeat it. Instead of leaving the crude base in dilute sulphuric acid for the purpose of purification, it was found more convenient to dissolve the dry product in a small quantity of benzene and precipitate the tar with petroleum ether (80–100°), the decanted liquid being then treated with further quantities of petroleum until crystals alone separate.

The conversion of peri-nitronaphthylamine into 8-nitro-1-naphthylazoinide proceeded in the normal fashion, and the product was purified twice from hot acetone, which deposits hard, lustrous, glass prisms, melting at 130–131° with decomposition; the substance is extremely sensitive to light, the crystals becoming pink in a few minutes' exposure:

1.50 gave 29.0 c.c. of nitrogen at 22° and 747 mm.  $N = 26.39$ .

$C_{10}H_6O_2N_4$  requires  $N = 26.16$  per cent.

Having in view the possibility of obtaining the peroxide of peri-naphthonedioxime, the azoinide was heated in boiling glacial acetic acid, in xylene, and in aniline, but in no case did the required reaction take place. Moreover, continued boiling with alcoholic potassium hydroxide to eliminate hydrazoic acid, the azoinide being rapidly converted into unrecognisable products of complete decomposition.



As in the case of  $\alpha$ -naphthylamine, we compared the commoner method of converting the base into the azoinide, finding as before that the process is comparable for convenience and cleanliness with

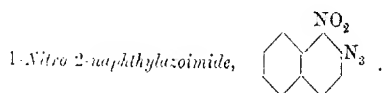


that of Noehling and Michel. The application of the hydroxyazo method to  $\beta$ -naphthylamine, however, was more successful than in the case of the isomeric substance, and a yield of 50 per cent. was obtained instead of only 5 per cent.; the remainder would appear to have been converted into 2:2-azoxynaphthalene, obtained by Meisenheimer. While by reducing 2-nitronaphthalene with sodium stannite (Beckmann, 36, 1165). The hydrazine method gave about 20 per cent. of product, which was not a good specimen, and ultimately the azoimide was prepared by adding sodium azide to diazotised  $\beta$ -naphthylamine in the presence of cyanamide, the quantities employed being the same as already mentioned for  $\alpha$ -naphthylazoimide. After steam distilling, which proceeds very slowly, the dried product was mixed with a quantity of petroleum and cooled in ice, when the azoimide crystallised in lustrous needles melting at  $33^\circ$ :

0.2486 gave 53.4 c.c. of nitrogen at  $21^\circ$  and 761 mm.  $N = 24.7$

$C_{10}H_7N_3$  requires  $N = 24.85$  per cent.

$\beta$ -Naphthylazoimide has the odour of ethoxynaphthalene; it is less sensitive to light than the nitro-derivatives, becoming yellow on continued exposure. The substance is freely soluble in organic solvents, dissolving less readily in methyl and ethyl alcohols, from which, however, it cannot be crystallised, as it separates as an oil on diluting with water; boiling water dissolves it very sparingly, and dilute solutions deposit lustrous, colourless leaflets resembling  $\beta$ -naphthylamine. Moderate concentrated sulphuric acid (55 per cent.) liberates two-thirds of azide nitrogen (16.18 per cent. instead of the calculated 16.52 per cent.), but it has not been possible to recognise the corresponding aminonaphthol in the product. Alcoholic potash does not eliminate hydrazoic acid.



This compound has been obtained by direct nitration of  $\beta$ -naphthylazoimide with acid of sp. gr. 1.12, and also by the action of hydrazoic acid on diazotised 1-nitro-2-naphthylamine; it was recrystallised twice from acetone, which deposited pale yellow, silky needles melting at  $116-117^\circ$  with vigorous gas evolution:

0.1556 gave 35.8 c.c. of nitrogen at  $21^\circ$  and 756 mm.  $N = 26.17$

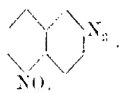
$C_{10}H_6O_2N_4$  requires  $N = 26.16$  per cent.

When reduced with alcoholic ammonium sulphide, a quantitative yield of 1-nitro-2-naphthylamine was obtained, m. p.  $124-125^\circ$ . Eighty per cent. sulphuric acid liberated two-thirds of the azide nitrogen (12.47 per cent. instead of the calculated 13.08 per cent.).

*Preparation by Heat.*—The readiness with which the substance decomposes precludes the use of alcohol or solvents of higher boiling point for crystallisation; a solution in glacial acetic acid undergoes decomposition at 50°, but as the temperature rises above this point, gas is evolved in quickly augmenting proportions, the effervescence being violent at 110°. When this change is complete, dilution with water precipitates the peroxide of  $\beta$ -naphthaquinonedioxime, which is obtained much more readily from the 1-nitro-2-azoimide than from isomeric 2-nitro-1-azoimide.

*Analysis.*—Twelve grams were heated with 100 c.c. of 1 per cent. alcoholic potash in a reflux apparatus during eight hours: during the dark red liquid, lustrous needles of the dioxime peroxide appeared. The residue from the evaporated liquid was taken up with water, filtered from a further quantity of the dioxime peroxide, dried with a small proportion of a substance which was not identified, and distilled in steam, when hydrazoic acid corresponding to 70 per cent. of the amount required by theory was obtained.

5-Nitro-2-naphthylazoimide,

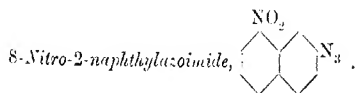


5-Nitro-2-naphthylamine employed in this preparation was obtained in association with a smaller proportion of 8-nitro-2-naphthylamine by the process of Friedländer and Szymanski (*Ber.*, 1892, **25**), which consists in adding  $\beta$ -naphthylamine nitrate to concentrated sulphuric acid at  $-10^\circ$ . The azoimide prepared from the named base was obtained from acetone in lustrous, brownish-red needles melting at  $133.5^\circ$ .

0.223 gave 43.8 c.c. of nitrogen at  $18^\circ$  and 744 mm.  $N = 26.16$ .

$C_{16}H_9O_2N_4$  requires  $N = 26.16$  per cent.

The substance is readily soluble in hot methyl and ethyl alcohols, and very freely in ethyl acetate and in glacial acetic acid. There is no sign of gas evolution when the solutions are heated, and hot alcoholic potash has failed to eliminate hydrazoic acid.



In production of this derivative from 8-nitro-2-naphthylamine proceeded smoothly, the conversion of the diazonium salt into nitrobenzene as in the case of all described in this paper, being

quantitative. Crystallisation from dilute acetone gave long yellow prisms melting at  $108^{\circ}$ :

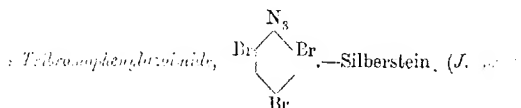
0.1321 gave 30.8 c.c. of nitrogen at  $23^{\circ}$  and 744 mm.  $N = 26.1$  per cent.  
 $C_{10}H_6O_2N_2$  requires  $N = 26.16$  per cent.

It was not possible to detect hydrazoic acid as a product of the reaction of 8-naphthylazoinide with alcoholic potash, and there was a tendency to pass into a di-oxime peroxide on heating the product alone.

#### *Preparation of Substituted Azoinides According to Noeling and Michel*

In working through the series just described, it has appeared that the regularity of the method first described by Noeling and Michel (*Ber.*, 1893, **26**, 86) is very significant. The generalization which has been recognised as connecting the triazo-group with halogens receives further confirmation from this reaction, and would seem to be applicable to any base capable of undergoing conversion into a diazonium salt, always provided that free nitric acid has no action on the resulting azoinide, a clause which prevents its use in the case of ortho- and para-hydroxyphenylazoinides (vol., 855 and 1350). In dealing with complex bases likely to undergo undesirable alteration when the diazonium salts are treated with bromine followed by ammonia, the method is invaluable.

Two examples of its application to delicate cases may be cited, those already described.




1883, [ii], **27**, 113) claims to have prepared this compound by dissolving tribromobenzene-diazonium nitrate dissolved in concentrated hydrochloric acid until crystals separate—these crystals being regarded as “tribromobenzene-diazonium chloride perbromide”—and treating the product with ammonia; no bromine was added, and it is to be presumed that this halogen was regarded as arising by decarboxylation of a portion of the tribromobenzene-diazonium salt. He obtained tribromophenylazoinide produced in this way as forming colorless needles melting at  $59^{\circ}$ . We think, however, that Silberstein has another substance in hand, because the product obtained by diazotising tribromoaniline and hydrazoic acid crystallises from water in long, lustrous, colorless needles, melting at  $72^{\circ}$ , and quickly becoming pink when exposed to light:

0.5621 gave 18.7 c.c. of nitrogen at 24° and 772 mm.  $N = 12.03$ .

$C_6H_4N_4$  requires  $N = 11.83$ ; Br = 67.00.

$C_6H_4Br_2N_4$  requires  $N = 11.83$ ; Br = 67.38 per cent.

According to the statement of Silberstein, the substance is not volatile at 100°.

 Six grams of *m*-picrylenediamine

and 1.5 g. of sodium azide were dissolved in 50 c.c. of 50 per cent. sulphuric acid, mixed with 4 grams of sodium azide; 6 grams of sodium nitrite were added to the ice-cold liquid, followed by a further 4 grams of sodium azide. After one hour, the emulsion was extracted with ether, the residue left by this on evaporation was distilled twice in steam. *p*-Bis(triazolene)benzene forms long, lustrous, faintly yellow needles, m.p. 57°; when heated quickly on a spatula, it does not explode, concentrated sulphuric acid gives a brilliant flame, accompanied by detonation.

From the recorded description of *p*-bis(triazolene)benzene (Griess, *Ber.*, 21, 1561; Silberrad, *Trans.*, 1906, 89, 171), it is evident that this compound is much less dangerous; a direct determination of *p*-benzotriazole was made without mishap by mixing the substance in a test-tube with potassium dichromate and copper oxide, the tube was then enclosed in a roll of oxidised copper gauze:

0.776 gave 59.6 c.c. of nitrogen at 23° and 743 mm.  $N = 52.73$ .

$C_6H_4N_6$  requires  $N = 52.50$  per cent.

In the foregoing experiment there was no detonation, but one attempt to estimate carbon and hydrogen was spoiled by a slight leak, which dispersed the vapour too rapidly in the tube without disturbing the apparatus; another combustion by the ordinary process was completed, but the carbon percentage was indicated at about 60 per cent. in excess of that required by theory, which is hardly surprising. Decomposition with 80 per cent. sulphuric acid gave results consistent with the usual behaviour of azoimides towards this reagent.

0.578 gave 56.4 c.c. of nitrogen at 22° and 767 mm.  $N = 53.26$ .

$C_6H_4N_6$  requires  $2/3 N = 53.04$  per cent.

*p*-Benzotriazole has a faint, but characteristic, odour of decayed fish; the inhaled vapour gives rise to a throbbing sensation at the base of the forehead.

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CXC. *The Action of Phosphorus Pentachloride on Hydroxytrimethylsuccinic Ester, 1:2-Dimethylcyclopropane-1:2-dicarboxylic Acid (1:2-methyltrimethylene-1:2-dicarboxylic Acid).*

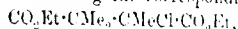
By HERBERT HENSTOCK and BERTHA ELIZABETH WOOLLEY

THE experiments described in this paper were undertaken at the request of Professor W. A. Bone, in order to clear up an important point of some interest, connected with the investigations on substituted succinic acids carried out by himself in conjunction with Mr. Sprankling and other collaborators (Trans., 1899, **75**, 830; **77**, 654, 1238; 1902, **81**, 50).

In one of their papers (Trans., 1902, **81**, 50), Bone and Spink described a methylenedimethylsuccinic acid,  $C_7H_{10}O_4$  (m. p. 130°), obtained by the action of diethylaniline on bromotrimethylsuccinic anhydride. The properties of this acid were subsequently examined by Bone and Henstock (Trans., 1903, **83**, 1380), and its inclusion as to its unsaturated character was confirmed by the detection of the magnetic rotation of its diethyl ester by the late William Perkin (*ibid.*, 1903, **83**, 1389).

In the year 1900, however, Paolini (*Gazzetta*, 1900, **30**, 61), following up the work of Kempf (*Act. Soc. Sc. Fennicae*, 1898, Abstr., 1899, i, 419), had described an isomeric acid,  $C_7H_{10}O_4$ , m. p. at 156°, obtained by a process (see below) which probably involved the elimination of hydrogen chloride from chlorotrimethylsuccinic ester. The fact that his acid neither decolorised cold potassium permanganate nor exhibited any tendency to form an addition compound with hydrogen bromide at the ordinary temperature led Paolini to regard it as a saturated compound, and he described it as 1:2-dimethyltrimethylene-1:2-dicarboxylic acid (1:2-dimethylcyclopropane-1:2-dicarboxylic acid). It seemed important to confirm Paolini's work and to examine the properties of his acid, the event of its cyclic character being confirmed, there would arise a remarkable difference in the behaviour of bromotrimethylsuccinic anhydride and chlorotrimethylsuccinic ester, under conditions favouring the elimination of the hydrogen halide. The starting point in the preparation of Paolini's acid is dimethylacetoacetic ester, which on treatment with hydrogen cyanide, according to the method of Kempf, and subsequent hydrolysis of the resulting cyanohydrin yields hydroxytrimethylsuccinic acid melting at 156–157°.

the acid is then subjected to the action of phosphorus pentachloride in chloroform solution. On pouring the liquid into cold water and then extracting with ether, an oil is obtained, which on treatment with alcoholic potash finally yields the acid under discussion. Here he stated that Komppa, who was the first to investigate the action of phosphorus pentachloride on diethyl hydroxytrimethylsuccinate, succeeded in isolating the corresponding chloro-derivative,



and we therefore must assume to be formed in the course of the present reactions. Komppa treated this chloro derivative with alcoholic potash and obtained a crystalline compound free from chlorine, which, on further examination, he assumed to be a  $\beta$ -lactonecarboxylic acid.

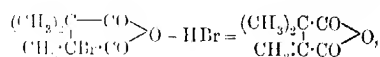
We have prepared Paolini's acid in considerable quantities and have made a thorough examination of its properties, the determination of its magnetic rotation of its diethyl ester having been undertaken by Sir William Perkin in March last. Although the investigation was not completed, we are able to state that the magnetic values of the diethyl ester left no doubt in his mind as to its isomeric character, and the contrast between its optical properties (magnetic rotation and refractive power) and those of the corresponding isomeric unsaturated ester obtained by Bone and Sprankling from trimethylsuccinic anhydride were, in his opinion, quite consistent with the saturated cyclic constitution which Paolini had assigned to his acid. The properties of the two isomeric acids and their diethyl esters may be tabulated as follows:

	<i>A.</i> Methylene dimethylsuccinic acid (Bone and Sprankling)	<i>B.</i> 1:2 Dimethylcyclopropane- 1:2 dicarboxylic acid (Paolini)
Boiling point .....	142.5°	119–150.5°
Specific rotation .....	0.01670	(Paolini gives 153°)
Appearance .....	Very soluble (cannot be recrystallised)	Less soluble than <i>A.</i> (can be readily recrystallised)
Refractive index .....	1.0199	1.9685
Magnetic rotation .....	1.0147	0.94381
Specific heat .....	11.925 } $t = 16.6$	10.5539 } $t = 18.9$
Specific heat .....	92.369	88.215
Specific heat .....	94.371	89.732
Specific heat .....	95.211	90.629
$H_f$ $H_a$ .....	2.881	2.375

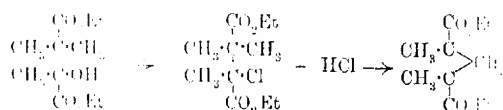
The structural difference between the two isomeric diethyl trimethylsuccinate under consideration is clearly brought out by a comparison of the calculated molecular rotations with the corresponding estimated value for trimethylsuccinate,  $C_{15}H_{22}O_4$ , namely, 11.205; the calculated value for the corresponding cyclic ester should be 0.6° lower, or (Trans., 1902, 81, 294). This is very near to the value for Paolini's ester (10.550). On the other hand, the calculated value for the corresponding unsaturated ester will, of course, be higher; that of diethyl trimethylsuccinate by 0.7° to 1.1°; the value for Bone and Sprinkling's ester (11.925), it will be seen, was 0.72° higher. The observed difference between the molecular refractive powers of the two esters is also in harmony with the supposed difference in structure, thus:

	Ha.	
	Calculated.	Found.
$C_{15}H_{22}O_4$ (Saturated) .....	59.80	58.24
Unsaturated .....	67.18	62.26
Difference .....	2.33	4.02

It must be admitted therefore that whereas in the case of trimethylsuccinic anhydride the elimination of hydrogen bromide by the action of diethylamine, gives rise to an unsaturated molecule,

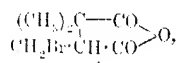


in Paolini's experiments hydrogen chloride was eliminated from chlorotrimethylsuccinic ester in such a manner as to yield a saturated compound, thus:



The reason for this difference in behaviour is not very apparent.

Experiments which are being carried out in these laboratories indicate that the bromo-anhydride may have the constitution



in which case the hydrogen atom marked with an asterisk is most likely to unite with the bromine atom when hydrogen bromide is eliminated, ring formation being thus precluded.

# EXPERIMENTAL.

## 1:2-Dimethylcyclopropane-1:2-dicarboxylic Acid.

The preparation of hydroxytrimethylsuccinic ester and of 1:2-dimethylcyclopropane-1:2-dicarboxylic acid was carried out according to the directions of Komppa (*Ber.*, 1896, 29, 1629) and Paolini (*Chim.*, 1904) and the yields compared very favourably with those obtained by other chemists.

Purity of the diethyl ester of the acid was prepared in the laboratory and its purity determined by analysis:

0.578 g. gave 0.3096  $\text{CO}_2$  and 0.1032  $\text{H}_2\text{O}$ .  $\text{C} = 61.63$ ;  $\text{H} = 8.40$ .  
 $\text{C}_{11}\text{H}_{18}\text{O}_4$  requires  $\text{C} = 61.68$ ;  $\text{H} = 8.40$  per cent.

Refractive and optical properties of this ester as determined by the Spectrometer of William Perkin were as follows:

$n_D^{20} = 1.0685$ .  $n_D^{15} = 1.0642$ .  $n_D^{20} - n_D^{15} = 0.0043$ .

Optical rotation:

$\alpha_D^{20}$	$\alpha_D^{15}$	$\alpha_D^{20} - \alpha_D^{15}$
$+18.9^\circ$	$+0.9138$	$+10.553$

Refractive power:

$d_{13}^{20} = 1.06363$ .

	Index of refraction, $\mu$ .	Sp. refraction, $\mu - 1^{\text{D}}$ .	Mol. refraction, $\mu - 1^{\text{D}}$ .
H ..... 1	1.43860	0.41256	88.245
H ..... 2	1.41660	0.41061	89.732
H ..... 3	1.45941	0.42346	100.629

Dispersion:  $\text{H}\gamma - \text{H}\alpha = 2.375$ .

On heating of the above values for the magnetic rotation and refractive power on the question of the constitution of the ester and its isomerism with methylenedimethylsuccinic acid, obtained by Bone and Sprinkling, has been discussed in the introductory portion of the paper (p. 1955).

1:2-Dimethylcyclopropane-1:2-dicarboxylic acid, after being reprecipitated from chloroform, melted at  $149-150.5^\circ$  (Paolini gives

0.560 g. gave 0.2240  $\text{CO}_2$  and 0.0675  $\text{H}_2\text{O}$ .  $\text{C} = 53.03$ ;  $\text{H} = 6.52$ .  
 $\text{C}_7\text{H}_{10}\text{O}_4$  requires  $\text{C} = 53.1$ ;  $\text{H} = 6.32$  per cent.

0.512 g. of the silver salt gave 0.3371 Ag.  $\text{Ag} = 58.12$ .

$\text{C}_7\text{H}_8\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 58.06$  per cent.

The physical and chemical properties agreed in nearly every respect with those described by Paolini.



The acid is very easily soluble in ether or alcohol, moderately in water, benzene, or chloroform, and insoluble in light petroleum. It yields an insoluble calcium salt, and also a liquid anhydride. It decolorises a dilute solution of alkaline permanganate in 10 minutes. The reason of this is that possibly the alkali breaks the ring, and is considerably weakened by the presence of the two  $\text{CH}_3$  groups. Evidence of this may be seen in the fact that the unsaturated methyl dimethyl-succinic acid decolorised alkaline permanganate instantaneously, whereas an equal weight of the *cyclopropane* acid requires one minute or two to produce the same effect.

The electrical conductivity at 25° was determined with the following results:

$$\mu_{\infty} = 360.$$

$c$ .	$\mu_{\infty}$ .	$m$ .	$K=100k$ .
25.42	17.86	0.0496	0.009859
52.84	24.83	0.0690	0.009989
165.68	35.69	0.0978	0.010149
211.36	48.64	0.1351	0.009985

$K=0.009993.$

Mixtures of this acid ( $\alpha$ ) with varying proportions of methyl dimethyl-succinic acid ( $\beta$ ), prepared by Bone and Sprankling, are as follows:

$\alpha$ .	$\beta$ .	M. p.
90 per cent.	10 per cent.	126°
10 "	90 "	136
50 "	50 "	128

The authors desire to express their best thanks to Professor Bone for his kind interest and help in the matter, and also to the Research Fund Committee of the Chemical Society for a grant which enabled them to purchase the more expensive chemicals used in the work.

They were also especially indebted to the late Sir William Bone for his great kindness in undertaking the determination of the properties of the ester, which so decisively proved its constitution.

THE UNIVERSITY,  
MANCHESTER.

*The Vapour Pressures of Triethylamine, of  
2:4:6-Trimethylpyridine, and of their Mixtures  
with Water.*

By ROBERT TABOR LATTEY.

I. *Triethylamine and Water.*

Work was undertaken in order to obtain experimental verification of the laws predicted by theory for the total and partial vapour pressure curves of two liquids, the miscibility of which depends on temperature. It was also hoped that a study of the properties of two liquids which are completely miscible at some temperatures and only partly soluble one in the other at other temperatures might throw light on the problem of the miscibility of fluids.

The forms of the vapour-pressure curves have been discussed by van Margules, Ostwald, Zawidzki, and others (for references, see Ostwald, *Trans.*, 1906, **89**, 1351 *et seq.*). The experiments were begun after the appearance of Marshall's paper (*loc. cit.*), and the discussion of the theoretical points, which was intended, has been consequently rendered unnecessary.

The following symbols are used throughout this paper:

$n$  = the ratio of the number of molecules of amine to the number of molecules of both kinds.

$p_a$  = the partial pressure of the amine vapour.

$p_w$  = the partial pressure of water vapour.

$p$  = the total vapour pressure of the mixture.

It has been shown by many previous authors:

$$\frac{p}{p_w} = \pi \frac{x}{1-x} \frac{dp_a}{dp_w} \quad \dots \dots \dots (i)$$

$$p_w^{1-x} p_a^x = \pi \quad \dots \dots \dots (ii)$$

$$\frac{dp_a}{dx} \cdot \frac{dp_w}{dx} = \frac{d\pi}{dx} \quad \dots \dots \dots (iii)$$

Consequently,

$$\frac{d\pi}{dx} (1-x) = \frac{dp_a}{dx} \left( 1 - x \frac{p_a}{p_w} \right) \quad \dots \dots \dots (iv).$$

A form of this equation (iv) is used by Marshall to deduce the relations of partial and total vapour-pressure curves. Both he (*Ann. Physik. Zeitsch.*, 1907, **8**, 347) and others suggest the use of equation (iv) in obtaining the values of the partial pressures when only the vapour pressures are known. The methods of both these authors consist in drawing probable curves, taking averages of the values of

$p_v$  and  $-x \frac{dp_v}{dx}$  obtained from these curves, and drawing through  $p_v$  approximate curves. A far simpler method is to use equation (1). From the total pressure curve, the values for  $\pi$  and  $\frac{d\pi}{dx}$  for values of  $x$  differing by 0.05 between  $x=0$  and  $x=1.00$  can be tabulated, the maximum,  $x = \frac{p_v}{\pi}$ , and consequently the value of  $p_v$  is known. In the neighbourhood of  $x=0$  and of  $x=1$ , the values of

$\frac{dp_v}{dx}$  are expressed graphically by straight lines joining the points  $(1, p_v)$  and  $(1.0)$  to  $(0, p_v)$  respectively.

An approximate curve for  $p_v$  can then be drawn and the values in the neighbourhood of known points be used to calculate  $\frac{dp_v}{dx}$ , and subsequently to correct the curvature in these neighbourhoods. It is surprising how easy the continuation of a curve once begun by this method becomes with a little practice. In portions of the curve where  $\frac{dp_v}{dx}$  is small,  $\frac{dp_v}{dx}$  can be taken as equal to  $10(p_1 - p_2)$ , where  $p_1$  and  $p_2$  are the values of  $p_v$  or of  $\pi$  for  $x+0.05$  and for  $x-0.05$  respectively. Since the curve representing the variations of  $\pi$  with changes in the value of  $x$  is drawn from experimental results, curvature will probably not be exactly determined at all points. The exact position of the maximum point, for instance, will probably not be known to within 1 or 2 per cent. If this is so, the values of  $\pi$  for  $p_v$  and  $p_v$  when  $x=0$  and when  $x=1$  will not be exact. Multiply each set of calculated partial pressures in the ratio  $p_v/\pi$  to obtain a correct end point and draw the total vapour-pressure curve so obtained alongside the original one. By this means, the position of errors in the original curve can be located and the necessary correction made. This operation can be repeated until satisfactory results are obtained. With an ordinarily well-determined total pressure curve this should not be more than once.

The vapour pressures of solutions of the following compounds were determined:

By dilution by mass: 0.00 1.05 4.30 10.45 23.34 41.69 81.75  
 0.0000000000 0.0000 0.0024 0.0091 0.0215 0.0515 0.113 0.222

From these and the vapour pressures of water given by the Goff and Teten curves were constructed and the values of  $p_v$  were calculated as indicated above. The values are given in Tables 1 and 2 shown by curves in Figs. 1, 2, and 3. At 22°, so much of the total

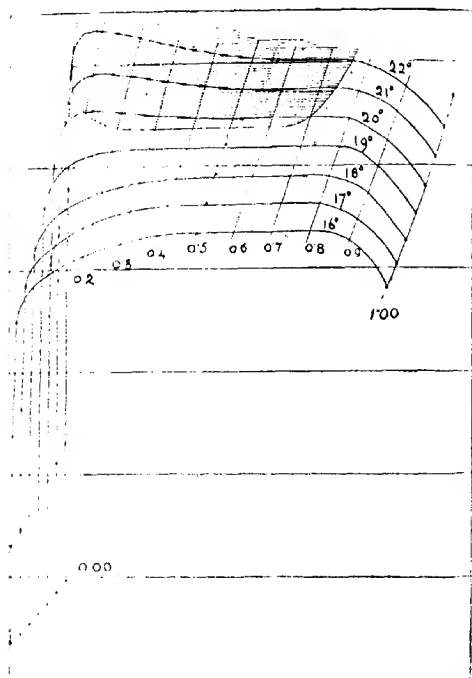
TABLE I.

$\lambda$	260 m $\mu$			280 m $\mu$			300 m $\mu$		
	$\pi$	$\rho_{\pi}$	$\rho_{\pi\pi}$	$\pi$	$\rho_{\pi}$	$\rho_{\pi\pi}$	$\pi$	$\rho_{\pi}$	$\rho_{\pi\pi}$
0.00	13.685	0.00	13.585	15.483	0.00	15.383	17.406	0.00	17.306
0.05	47.50	36.30	13.520	54.10	38.25	14.855	16.86	53.81	39.46
0.10	59.43	36.56	13.07	56.00	41.20	14.80	16.70	53.18	39.34
0.15	59.42	37.45	12.97	56.92	42.185	14.735	16.76	53.84	39.36
0.20	51.30	38.12	12.88	57.80	42.91	14.66	16.79	52.97	39.40
0.25	52.00	39.225	12.775	58.965	43.44	14.625	16.88	52.33	39.415
0.30	52.60	39.92	12.68	58.435	43.85	14.585	16.835	52.08	39.385
0.35	53.04	40.11	12.60	58.015	44.12	14.55	16.82	51.94	39.355
0.40	53.32	40.80	12.52	58.735	44.29	14.505	16.87	51.29	39.355
0.45	53.48	41.035	12.415	58.84	44.57	14.47	16.865	50.61	39.36
0.50	53.53	41.14	12.30	58.89	44.42	14.47	16.865	50.12	39.385
0.55	53.56	41.58	12.38	58.91	44.76	14.455	16.85	50.29	39.05
0.60	53.59	41.235	12.355	58.95	44.535	14.475	16.79	50.11	29.12
0.65	53.62	41.29	12.33	58.975	44.605	14.37	16.96	50.25	29.07
0.70	53.65	41.37	12.28	59.015	44.70	14.315	16.965	50.22	29.03
0.75	53.67	41.57	12.32	59.06	44.82	14.31	16.79	50.18	19.78
0.80	53.7	41.79	11.34	58.95	45.23	13.72	15.99	49.55	17.89
0.85	53.75	42.31	11.10	58.90	46.12	13.68	15.95	51.94	14.15
0.90	53.80	42.62	10.88	58.89	46.99	13.59	15.81	57.59	9.87
0.95	53.84	42.89	10.69	58.90	47.30	13.50	15.59	56.99	6.58
1.00	48.20	48.40	0.00	57.77	47.77	9.99	0.00	43.70	0.00

falls within the unreal portion (indicated by shading) that the value had to be largely obtained by extrapolation.

The gradual change in the type of the curves is obvious. At 16° the total pressure curve is of the common single-maximum type; the partial pressure curves are of Marshall's type 3; but as the temperature rises, the characters of the curves change, and

FIG. 1.—*Total Pressure Isotherms.*

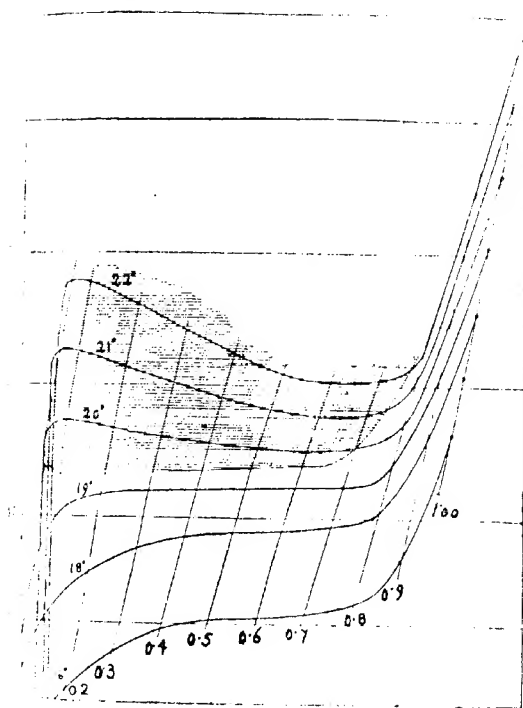


16° a flat portion appears in all. Above 19° each partial pressure curve has both a maximum and a minimum point, and each total pressure curve has two maxima; there is consequently an unreal portion in every curve, and this increases in length as the temperature rises.

If the total pressure is plotted against the composition of the vapour, instead of that of the liquid as is usual, the vapour-pressure

Roozeboom's "gas curves") assume the form shown in Fig. 4. If the azeotreal portion now assumes the form of a loop, it can readily be seen that the mixtures in equilibrium at 22° give a vapour the composition of which is given by  $x = 0.7226$ , and the vapour pressure by 62 mm. This corresponds to liquids for which  $x = 0.772$  and 0.020.

Fig. 2.—Partial Pressure of A and  $P_A/P_A^0$ .



From the curve, similar values were read off and the following results were obtained:

All concentrations are possible.

For 0.09 and 0.045,  $\pi = 64.60$  (64.45).\* Composition of vapour = 0.7380.

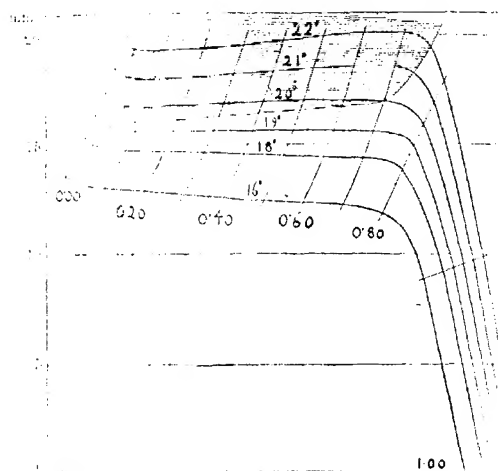
\* The figures in brackets are the means of experimental values.

21.  $x_2 = 0.737$  and  $0.03$ ,  $\pi = 67.87$  (67.30). Composition of  
0.7333.  
22.  $0.772$  and  $0.02$  70.11 (70.71). Composition of  
0.7226.

It will be seen that the total pressure curve at  $22^\circ$  belongs to a slightly different type from that at  $20^\circ$ , since both the maximum and higher temperature come within the unreal portion.

The values obtained from the equilibrium concentrations have been plotted against the temperature in Fig. 5. Some of Rothmund's and Guthrie's direct observations on the separation of mixtures

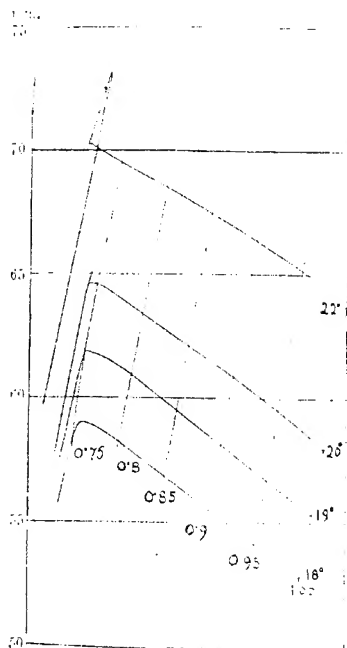
Fig. 6. Partial Pressure of Water Vapour.



of triethylamine and water have been plotted in the same figure (*Z. physikal. Chem.*, 1898, 26, 433; *Phil. Mag.*, 1884, [v], 18, 501). Most serious discrepancies appear in the neighbourhood of  $x_2 = 0.5$ . There are probably two reasons for this: (i) this is the region in which it is most difficult to obtain results from the vapour-pressure curves, and (ii) most of the observations are by Guthrie (1906). The remainder of his observations were shown by Rothmund (*loc. cit.*) to be not only inaccurate, but impossible. From the curves, it will be seen that the vapours in contact with the equilibrium mixtures at 22 and  $21^\circ$  should have pressures  $p_H = 50.66$  and  $p_H = 19.45$ . A direct determination of the partial pressure of the amine vapour was therefore made at

are by the Earl of Berkeley and E. J. G. Hartley's modification of the ebullioscopic method. The vapours carried over by 20 litres of air passed through dilute sulphuric acid and so analysed. The values for  $p_v$  were 50.07 and 51.38 mm. in two separate experiments giving an average value 50.73 mm. The agreement is satisfactory considering the somewhat inaccurate calculation on which one result

FIG. 1.



## II. 2:4:6-Trimethylpyridine. ( $\gamma$ -Collidine).

The solubilities of this compound and of water have been determined by Rothmund (*loc. cit.*). It was hoped that, since the solubilities of water and trimethylpyridine are greater than those of water and triethylamine, this pair would prove more suitable for the purposes of this investigation. The extremely small vapour pressure of trimethylpyridine at the ordinary temperature rendered the results liable to large percentage errors and so unsuitable for quantitative analysis.

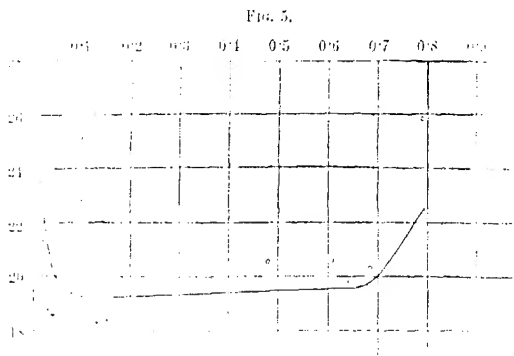


2:4:6-Trimethylpyridinedicarboxylic ester was prepared by Hantzsch's method (*Annalen*, 1882, **215**, 1) and simultaneously hydrolysed and deprived of the carboxylic groups by heating with sodium (Mai and Aicheff, *Ber.*, 1892, **25**, 374).

The total pressures of the solutions were determined in the same way as were those of triethylamine, with the exception of the case for which  $x = 0.1745$ , which was compared with pure water in a manometer.

The total pressure curves are of exactly the same type as those obtained for mixtures of triethylamine and water. The results of measurements are given in Table 3.

As might have been expected, the isotherms for both triethylamine-water mixtures and for trimethylpyridine-water mixtures are of



striking resemblance to those obtained by Zawidzki for pyridine-water (*Z. physikal. Chem.*, 1900, **35**, 196), and to those obtained by Schreinemakers (*ibid.*, 474) for aniline-water mixtures.

## EXPERIMENTAL.

### Total Pressures.

The apparatus used for determining total pressures is shown in Fig. 6. After being cleaned and dried, it was immersed to the top of the tap *B* in a bath having glass sides, and was sealed to a bath containing phosphorus pentoxide connected with a Töpfer pump. The apparatus was then exhausted and left overnight with all taps closed. When it was judged that the inside of the apparatus was fairly dry, tap *B* was opened and mercury was poured in until

slightly more than sufficient quantity to fill the tube between *A* and *B*. The cup was then exhausted through a tube passing through a rubber plug placed in the top of the cup. *B* was then closed by opening *A* part of the mercury above it was allowed to pass to the apparatus; this amount of mercury was not sufficient to fill the apparatus at the bottom. The pump was worked carefully. By this means a column of mercury free from bubbles was obtained in the lower part of the tube between *A* and *B*. The tap *B* was now opened, and air admitted to the cup, which was then filled with mercury. By opening *A* and *B* alternately, it was possible to get either mercury or a vacuum in the upper part of the tube between them. No considerable amount of air was thus carried into the bulb *C* or the mercury.

When sufficient mercury had been let in, the tap was stopped and air admitted to the bulb *C*. As the mercury rising in *C* passed the T join, tap *A* was turned and any air imprisoned in the mercury consequently driven into the space between *A* and *B*. *C* was then evacuated, the operation repeated.

The liquid, the vapour pressure of which was to be measured, was then placed in the cup. Finally all the mercury between *A* and *B* was allowed to run down into *C*, the liquid being drawn into the space so evacuated. When the space between *B* and *A* was full of liquid, tap *B* was closed, and a few drops of mercury were blown into the tube above it. The liquid was then admitted to *C*, where it floated on the surface of the mercury.\*

The difference in level of the mercury surfaces *A* and *E* could then be read by means of a cathetometer and a glass scale.

The apparatus has three advantages over most other apparatus for the same purpose. (i) Both mercury surfaces are in glass tubes of the same gauge, and there is consequently no correction for capillarity; (ii) both surfaces are dry, and (iii) the level in *E* alters very little in level when the mercury rises considerably in *B*; this greatly reduces the necessary number of readings.

The tubes were lubricated with vaslin and indiarubber; *A* was provided with a stopper of both oils, and the tube between the taps was always partly filled with oil. No oil readings were being made.

FIG. 6.

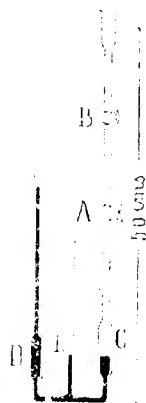


TABLE II.  
Vapour Pressures of Triethylamine and Water.

$t$ , °C.	100.0	110.0	120.0	130.0	140.0	150.0	160.0	170.0	180.0	190.0	200.0	210.0	220.0	230.0	240.0	250.0	260.0	270.0	280.0	290.0	300.0
7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
10	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
14	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
16	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
17	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
18	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
19	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
21	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
22	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
23	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
24	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
25	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
26	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
27	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
28	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
29	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
30	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

THE PART OF THIS TABLE WHICH RELATES TO THE VAPOUR PRESSURES OF WATER IS FROM THE LITERATURE.

Observations were then made at intervals of about 0.2° at temperatures ranging between 7° and 50°; all sudden or rapid changes of temperature were avoided.

A complete set of observations was then smoothed by the use of the following equation:

$$At = \log p - B,$$

where  $A$  and  $B$  are constants. A suitable value for  $B$  was chosen, and the values of  $A$  calculated for each observation separately. The values for  $A$  were then plotted against  $t$  on squared paper and a smooth curve drawn. The values of  $A$  were then read off for the entire range over the experimental range. The values for  $p$  thus obtained were corrected for the expansion of mercury.

In order to test the accuracy of the apparatus, two sets of observations were made with water. These gave the following results:

$t$	16.40 (15.868)	17	17.18 (17.187)
	16.81 (16.167)	14	17.70 (17.356)
$p$	17.22 (17.880)	15	18.36 (18.728)
	17.66 (17.406)	16	19.11 (19.565)
	18.07 (17.947)	17	19.98 (19.459)
	18.48 (18.503)	18	21.02 (21.383)
		19	22.06 (22.367)
		20	23.11 (23.196)

The figures in brackets are taken from Luedolt and Bornstein's tables for comparison.

TABLE III.

*Vapor Pressures of 2:4:6-Trimethylpyridine and its Solutions in Water.*

$t$	6.	52.00.	58.68.	85.74.	95.8.	98.7.	100.
$p$	0.004.	0.113.	0.1745.	0.472.	0.7715.	0.9185.	1.000.
$x$	0.1	0.8	—	—	—	—	2.7
	12.7	13.9	13.1	—	10.1	7.9	3.3
	18.2	17.6	17.85	17.5	14.3	10.9	4.1
	21.6	21.2	21.1	14.4	19.3	15.1	5.3
	30.1	32.3	32.3	32.9	26.6	26.8	6.3
	41.2	43.4	42.9	43.2	36.1	38.7	7.7
	55.7	56.3	56.15	57.9	42.9	38.1	9.4
	74.8	71.1	73.6	74.8	65.6	50.5	11.7
	96.1	95.2	95.9	96.9	85.8	67.2	14.8
	122.3	129.9	121.9	124.9	111.5	87.1	18.9
	—	—	—	—	—	—	23.8
	—	—	—	—	—	—	31.9

\* Part of the table enclosed in heavy lines refers to temperatures above 50°; the solubilities are only partial.

The apparatus was taken down, set up as before, and similar experiments were made with triethylaminé (Kahlbaum) freshly distilled (potash 5b, p. 882; 884 under 747.8 mm. pressure). The results are given on p. 1971. Solutions of various concentrations were examined; the vapour pressures of these are given in Table II.

#### *Partial Pressure.*

The partial pressure of triethylamine over the equilibrium mixture 22 was measured by a slight modification of the Earl of Berkeley and E. J. G. Hartley's method (*Proc. Roy. Soc.*, 1906, **77**, 150). Air freed from carbon dioxide and moisture by passing through towers containing potash and soda-lime was drawn through three weighed tubes containing (i) the amine-water mixtures, (ii) 30 c.c. of 2.516*N* sulphuric acid, and (iii) concentrated sulphuric acid. The tubes were situated in a thermostat in such a way that their inner surfaces were continually wetted with the contained liquid.

When the aspirator, which held 20 litres, was empty of water, the tubes were removed, disconnected, washed, and left with stoppers in boxes containing trays of calcium chloride. They were subsequently weighed.

The dilute acid in tube (ii) was then washed out and titrated with *N*-sodium carbonate solution. From this the mass of amine carried over by the air could be calculated. From the difference between the weight and the loss in weight of the tube (i) - or the united tubes (ii) and (iii) - the mass of water vapour could be obtained. The use of the tubes makes accurate weighing on an ordinary balance impossible; even when the tube can be placed on the pan it is liable to tilt, owing to the flow of liquid to one end (Berkeley and Hartley used a specially constructed balance). In making the calculations it has been assumed that the partial pressure of water vapour over the solution is 10.12 mm. at 22°. If the vapour pressure of the water is entirely neglected, the pressure calculated for the amine vapour will be raised by 1.26 mm.; an error of several millimetres in the value assumed for  $p_w$  will not therefore make a very serious error in  $p_a$ .

Two experiments were made and yielded the following results:

Mass of amine in grams	Volume of air, corrected to N.T.P. in litres	Height of barometer in mm.	Duration of experi- ment, in hours.	$p_a$ mm.
6.507	18.924	756	16.5	50.7
6.49.4	18.766	753	21.5	50.7

In the second experiment, tubes (i) and (ii) were partly filled with hollow glass beads.

The mean result is  $p_a = 50.73$  mm.

kindest thanks are due and gratefully rendered to Dr. H. G. Baker and the Governing Body for allowing me to carry out experiments in Christ Church laboratory.

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### XXII.—*Liquid Triethylamine.*

By ROBERT TABOR LATTEY.

Molar latent heat of triethylamine calculated from the vapour pressure and its rate of change with change of temperature give values ranging from 7100 Cal. at 14° to 8160 Cal. at 49°. In the case of liquids, the latent heat decreases with rising temperature; this behaviour is noticed in the case of acetic acid (Roozeboom, *see Gleichgewichte*, I, 52), and indicates a difference in the nature of the gaseous and liquid phases.

The difference in the case of triethylamine is small (see Table I) and

TABLE I.

Vapour pressure.	$dP/dT$ .	$q \times 10^{-3}$ .	Temp.	Vapour pressure.	$dP/dT$ .	$q \times 10^{-3}$ .
7.97	—	—	31	16.59	1.235	80.8
15.82	1.515	61.7	32	16.69	1.165	80.8
18.49	1.655	65.1	33	16.923	1.695	80.3
22.13	1.735	68.2	34	16.96	1.785	80.1
25.93	1.93	70.8	35	17.189	1.97	80.5
29.99	2.06	72.8	36	17.84	5.15	80.5
35.41	2.19	74.5	37	18.519	5.655	80.6
42.67	2.33	76.2	38	19.555	5.55	80.7
52.77	2.465	77.5	39	19.929	5.75	80.6
65.63	2.585	78.4	40	19.96	6.90	81.1
81.36	2.73	79.2	41	19.929	6.25	81.5
99.76	2.87	80.0	42	15.455	6.15	81.2
121.9	3.005	80.1	43	16.1	6.725	81.7
148.77	3.135	80.6	44	16.89	6.95	81.5
180.97	3.265	80.6	45	17.59	7.2	81.5
219.1	3.49	80.7	46	18.24	7.45	81.5
267.77	3.515	80.9	47	18.99	7.725	81.6
328.29	3.685	80.8	48	19.785	8.00	81.6
394.1	3.825	80.7	49	20.59	8.275	81.6
467.1	3.98	80.8	50	21.41	—	—
548.3	4.13	80.6	—	—	—	—

possibly be due to experimental errors. It seemed, however, worthwhile to investigate some of the properties more closely in order to determine which of the two explanations was the more

In Table II are compared the vapour pressures of triethylamine,

TABLE II.

		Vapour pressures at corresponding temperatures = $P$				$P/P_c$		
$T$	$T_c$	Hexane	Amine	Alcohol	Water	Hexane	Amine	Alcohol
100°	234.8°	267.5	233.6	358.1	—	1.0669	1.0690	1.8600
150°	234.8	285.0	249.0	489.0	1185.8	0.9329	0.9333	0.6722
200°	234.8	320.4	270	696	3581	0.8082	0.9304	0.3822
250°	234.8	348.4	284.4	896	875.6	0.7655	0.9290	0.2822
300°	234.8	369.32	293.2	1094	245.8	0.7237	0.9276	0.2067
350°	234.8	383.67	299.1	1249	336.5	0.6933	0.9267	0.1567
400°	234.8	391.32	303.1	1365	435	0.6629	0.9262	0.1167

hexane, ethyl alcohol, and water. The necessary data were taken from Landolt and Börnstein's tables. When the values of the ratio of the vapour pressure to the critical pressure for the amine are compared with the ratios obtained at corresponding temperatures for the other three liquids, it is at once clear that the behaviour of the amine is far more nearly akin to that of the unimolecular liquids than to that of either of the typical associated liquids, alcohol and water.

A comparison of the molecular latent heats,  $q$ , at various temperatures with those of other liquids at corresponding temperatures leads to the same conclusion.

The values are given in Table III, and were calculated from the

TABLE III.

$T$	Hexane		Amine		Alcohol		Water	
	$q/T_c$	$q/T$	$q/10^3$	$q/T_c$	$q/10^3$	$q/T_c$	$q/10^3$	$q/T_c$
100°	723	213.1	—	20.0	—	26.1	—	—
150°	719.6	219.6	81.6	25.25	—	—	95.9	—
200°	716.4	225.7	89.6	29.7	109.7	33.8	97.8	—
250°	713.8	229.8	89.7	29.8	98.9	34.6	99.4	—
300°	711.3	233.0	76.2	26.3	95.0	34.2	100.5	—

formula:  $\frac{dP}{dT} = \frac{0.5102P}{P_c} q$ , except in the case of water. The

were confirmed by an examination of the molecular surface tensions. The surface tensions of triethylamine at 11° and at 30° were compared with those of water at the same temperatures by comparing the pressures necessary to force a bubble of air from a capillary tube immersed in the fluid (Whatmough, *Zeitsch. physikal. Chemie.*, 129). In connexion with these experiments, my thanks are due to Mr. H. B. Hartley, of Balliol College, for kindly placing at my disposal his apparatus for these determinations and a great deal of kind help.

and the surface tensions of water at 11° and 30° as 71.83 and 68.48 dynes per sq. cm. respectively (Lundolt and Börnstein), the above results were obtained for triethylamine.

$\gamma$	$\gamma_{10^\circ}$	$\gamma_{30^\circ}$	$\gamma_{40^\circ}$
71.83	25.13	27.61	25.64
68.48	25.47	27.25	25.05
70.70	25.61	27.43	25.34
	Mean .....	27.70	25.97

The molecular volumes for these temperatures were calculated from density determinations made by Sir W. H. Perkin (Trans., 1889, 109), as 137.12 and 139.32 respectively. From these the molecular surface energies,  $\alpha = \gamma v^{\frac{2}{3}}$ , were calculated to be 736.4 at 11° and 681.7 at 30°. The temperature coefficient,  $\frac{d\alpha}{dt}$ , is therefore 2.879, and the critical temperature calculated by Ramsay and Young's method is  $39^\circ + 6^\circ = 272.8^\circ$ . Pawlewski (*Der.*, 1883, 16, 2633) gives 272.5°, and Vincent and Chappuis (*Compt. rend.*, 1886, 103, 379) give 272.6°, the value of  $T_x$ .

As associated liquids give values for  $\frac{d\alpha}{dt}$  less than 2.121, it is improbable that triethylamine is associated.

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### III.—*The Alcohols of the Hydroaromatic and Terpene Series. Part I. Resolution of the Alcohols into their Optically Active Components and the Preparation of the Borneols.*

by ROBERT HOWSON PICKARD and WILLIAM OSWALD LITTLEBURY.

#### *Introduction.*

Some of the problems still awaiting solution in the terpene and hydroaromatic series are connected with the alcohols of this class of compounds. Such, for example, are the questions of the relation of *bornyl* to *isoborneol*; of fenchol to *isofenchol*; between the various "camphens" and "fenchenes"; between the various menthols; and the problem of the isolation in a pure state and determination of the constitution of the stereoisomerides formed in the reduction of camphor by the splendid catalytic method of Sabatier and Berthelot.

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The confusion existing in the literature on several of these questions appears to us to be caused partly by investigations carried out on impure materials. Now, since nearly all the alcohols in question are either optically active or contain one or more asymmetric carbon atoms in the molecule, it is obvious that the first step in a re-investigation of these problems is to discover a method, or methods, which will lead to the purification of the alcohols with regard to their specific rotation, and also of the resolution of the synthetic or otherwise inactive compounds into their optically active components.

Such a method, it was hoped, would be the preparation and fractional crystallisation of the *l*-menthylcarbamates previously described (Trans., 1904, 85, 685; 1906, 89, 93, 467, 1254). This method, however, is not always applicable; thus, to take a few examples, *d*- and *l*-isobornyl *l*-menthylcarbamates, prepared from *isobornyl* ("camphene") and *l*-menthylcarbinide, seem to form mixed crystals inseparable by fractional crystallisation, whilst the *l*-menthylcarbamate of 1:3-methylcyclohexanol is a viscous oil.

The problem has been solved in a more simple manner, and the alcohols can be resolved into their optically active components by the method described below, which appears to be quite a general one. It has been applied, not only in the cases indicated above, but also to alcohols of simpler constitution. There are three stages in the process. Firstly, the alcohol is converted into the hydrogen ester of a polybasic acid by heating with the anhydride of the same. For this purpose, phthalic and succinic anhydrides are well adapted, and in some cases the compounds required have been already described. For example, the bornyl hydrogen phthalates (Haller, *Compt. rend. acad. sci. Paris*, 1908, 456) and  $\beta$  thymomenthyl hydrogen phthalate (Brunel, *Compt. rend.*, 1905, 140, 252). Secondly, these acid esters, for example,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{R}$ , are resolved by a strong optically active base according to Pasteur's method. In some cases, the commoner alkalis suffice for the purpose, in others it is necessary to use *l*-menthylamine, which is a strong base and very serviceable for the resolution of acids, as has been pointed out by one of us and collaborators (Trans., 1905, 87, 1763; 1906, 89, 384 and 1101). Thirdly, the pure optically active acid ester is hydrolysed. The hydrolysis is, as a rule, effected by warming with the calculated amount of alcoholic potassium hydroxide, or even by merely boiling an aqueous solution of the potassium salt of the acid ester (compare Haller, *loc. cit.*). The ease with which this third stage is accomplished renders this new method preferable to our first method, since some of the *l*-menthylcarbamates are very difficultly hydrolysed with extraordinary difficulty under conditions tending to racemisation. The new method, moreover, has the further advantage

particular allows of the preparation of the two components, whereas the methylcarbamide method generally yields only the one.

The underlying idea of the method does not seem altogether new. The Krieger (*Ber.*, 1893, **26**, 1203) appears to have attempted, unsuccessfully, the resolution of methylpropylcarbinyl hydrogen sulphate by means of the strychnine salt, whilst, during the course of this work, Gell (*Ber.*, 1907, **40**, 695) described a resolution of *sec.*-butyl alcohol by an analogous method. Meth's process includes the preparation of hydrogen sulphuric ester, and the use of sulphuric acid is, of course, impossible, except in the case of the most stable alcohols, on account of its strong dehydrating action.

The present communication describes the preparation of *d*- and *l*-camphor and *d*- and *l*-isoborneol, and, it is hoped, will be followed up by others dealing with the problems indicated above.

#### *Borneol and isoBorneol.*

*d*- and *l*-Borneols were prepared in a state of purity by Haller, and described by him under the name of camphols (*Ann. Chim. Phys.*, 1855, [vi], **27**, 424). Recently, the separation of these two other isomerides (*isoborneols*) has been described by Tschugaeff (*Russ. Phys. Chem. Soc.*, 1904, **36**, 1096), who showed that the *l*-bornylxanthates, but not the *isobornyl* esters, when hydrolysed, give the corresponding alcohols. The borneols described by Tschugaeff had a slightly higher rotation than those of Haller. We have prepared pure borneols by three methods, each of which yielded products of practically identical rotation to those given by Haller, namely: (i) by Tschugaeff's method; (ii) by fractional crystallisation and subsequent hydrolysis of *l*-bornyl *l*-menthylcarbamate, and (iii) by ester treatment of the *l*-menthylamine salts of *d*- and *l*-bornyl hydrogen phthalates.

*l*-Bornyl hydrogen phthalate is readily prepared by the action of phthalic anhydride on the inactive *isoborneol* obtained by the hydrolysis of its acetate, which is formed when camphene is treated with acetic and sulphuric acids (Bertram and Walbaum, *J. pr. Chem.*, 1904, [3], **49**, 15). It is readily resolved by *l*-menthylamine, the *l*-bornyl component being less soluble in dilute alcohol; whilst the *d*-bornyl component is obtained by crystallising the *d*-cinchonine salt, as the *d*-*l*-component is the less soluble in alcohol. From these salts the *d*- and *l*-isobornyl hydrogen phthalates have been obtained, which when hydrolysed, yield the pure *d*- and *l*-isoborneols. These have rotations approximately  $[\alpha]_D \pm 34.3^\circ$  in ethyl-alcoholic solution, and when oxidised give pure camphor with a specific rotation of

opposite sign. Haller's isocamphols had  $[\alpha]_D = 32.9^\circ$  in 95% alcoholic solution.

Our results therefore confirm Haller's work on the camphols, prove the truth of the suggestion (Bertram and Walbaum, 1922) that his isocamphols are identical with isoborneol. We would, however, point out that it is by no means certain that "isoborneol" prepared from camphene contains only *d*- and *l*-isoborneols. The method described in this paper allows of the easy preparation of pure isoborneols in quantity, and will afford material for the investigation of the relationship between borneol and its isomers.

#### EXPERIMENTAL

*Borneol*.—The crude *l*-borneol used in our experiments was obtained from Schimmel, and after one crystallisation from light petroleum,  $[\alpha]_D = 37.1$  in toluene with  $c^* = 11.5$ . Fifty grams of this were converted by Tschugaeff's method (*loc. cit.*) into methyl *l*-bornylcarbamate  $\text{CH}_3\text{OOC}\cdot\text{C}_9\text{H}_{17}$ .

The ester was distilled with steam and, after two crystallisations from dilute alcohol, melted at  $58^\circ$ . The borneol obtained from it, produced by hydrolysis with alcoholic sodium hydroxide was distilled with steam and crystallised from light petroleum. 2.3021 grams, up to 1.99 c.c. with toluene, gave  $a_D = 8.77^\circ$ , whence  $[\alpha]_D = 37.1$  ( $c = 11.5$ ). Tschugaeff gives  $[\alpha]_D = 38.23^\circ$  ( $c = 13.12$ ).

#### *Isolation of l-Borneol by Means of l-Menthylcarbinol*

##### *Preparation of l-Menthylcarbamate, $\text{C}_{10}\text{H}_{19}\cdot\text{NH}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{17}$*

Molecular quantities of *l*-menthylamine, *l*-bornyl chlorocarbonate and sodium hydrogen carbonate are mixed in toluene and heated on a water bath for three hours. The toluene solution, after washing with water and dilute hydrochloric acid, is distilled and the residue crystallised from dilute alcohol. After two crystallisations from dilute alcohol, the pure substance was obtained in long, colorless prismatic rods, which melted at  $136^\circ$ :

0.6688 gave 15.0 c.c. moist nitrogen at  $18^\circ$  and 747 mm.  $\text{N} = 1.4$ .

$\text{C}_{20}\text{H}_{37}\text{O}_2\text{N}$  requires  $\text{N} = 4.2$  per cent.

The specific rotation of the crude product was  $[\alpha]_D = 67.6$  in 95% alcoholic solution, and this, during the fractional crystallisation

<sup>1</sup> The number of molecules of oil in 100 c.c. of solution. All rotations in this paper were observed in a 2-dm. tube at  $15-18^\circ$ .

<sup>2</sup> *l*-Bornyl chlorocarbonate, b. p.  $130/35$  mm., is readily prepared by *l*-borneol distilled in toluene with the addition compound of carbonyl chloride and pyridine, compare D.R.P. 199,117,924.

came to the constant value  $[\alpha]_D = 71.04^\circ$  (with  $c$  between 2.5 and 4.0), whence  $[M]_D = 238.0^\circ$ .

*Hydrolysis of 1-Bornyl 1-Menthylcarbamate.*—The carbamate was hydrolysed under varying conditions. Two experiments only are here recorded. In the first, a large excess of sodium hydroxide was used; in the second,  $1\frac{1}{2}$  mol. only (2 molecules being theoretically required for complete hydrolysis). In each of these, the ester was put in a sealed tube with the alcoholic sodium hydroxide for five days at about  $140^\circ$ . The alcohol was then evaporated, the residue distilled, and the *l*-borneol distilled in a current of steam. After correction from light petroleum, the specific rotations of the *l*-borneol from the two experiments were determined:

First run: 2.3149, made up to 19.9 c.c. with toluene, gave  $\alpha = 8.55^\circ$ , whence  $[\alpha]_D = 37.96^\circ$  ( $c = 11.5$ ).

Second run: 2.3049, made up to 19.95 c.c. with toluene, gave  $\alpha = 8.76^\circ$ , whence  $[\alpha]_D = 37.92^\circ$ .

*Resolution of l-Borneol by Means of the 1-Menthylamine Salt of Bornyl Hydrogen Phthalate.*

The 1-*menthylamine* salt of bornyl hydrogen phthalate is readily obtained when an aqueous solution of 1-menthylamine hydrochloride (4 g.) is added to a neutral solution of the phthalate (1 mol.) in a solution of potassium carbonate. The precipitated pasty mass soon dries, and, after four crystallisations from dilute methyl alcohol, the *l*-salt is obtained in prismatic needles, melting at  $160^\circ$ , with a constant specific rotation in methyl alcohol of  $[\alpha]_D = 52.8^\circ$  with  $c = 5.0$ . The salt is decomposed by dilute hydrochloric acid, and the resulting bornyl hydrogen phthalate hydrolysed by boiling with alcoholic sodium hydroxide. The *l*-borneol thus obtained was crystallised once more from light petroleum, and had  $[\alpha]_D = 37.61^\circ$  in toluene solution with  $c = 10$ .

*d-Borneol from the Reduction Products of Camphor.*

Natural *d*-borneol is not readily obtainable. It may, however, be prepared from the commercial synthetic product prepared by the reduction of camphor. This seems to be composed of mixed crystals of *d*-borneol and 1-*isoborneol*, and has  $[\alpha]_D$  about  $+24^\circ$  in ethyl-alcohol solution. Pure *d*-borneol can be obtained from it by the following method (compare McKenzie, this vol., 1225): 100 grams of commercial product are dissolved in 80 grams of benzene, and added with 50 grams of zinc chloride for three hours. The solution is then washed with acidified water and fractionally distilled. The *d*-borneol thus obtained, after one crystallisation from light petroleum,

has  $[\alpha]_D^{20} +56.1$  in ethyl-alcoholic solution, and can be readily purified by conversion into the hydrogen phthalic ester and the *l*-menthylamine salt in the manner described above for *l*-borneol.

*d*-Borneyl hydrogen phthalate crystallises readily from glacial acetic acid in prismatic needles, and melts at  $164^\circ$ :

1.0059, made up to 19.85 c.c. with ethyl alcohol, gave  $\alpha +12.7$ , whence  $[\alpha]_D^{20} +56.7$ .

The *l*-menthylamine salt crystallises readily from acetone, and has  $[\alpha]_D^{20} +17.2$  in ethyl-alcoholic solution with  $c=5.0$ .

The *d*-borneol, obtained by the hydrolysis of this ester, was altered in specific rotation by crystallisation from light petroleum. Of the three following polarimetric observations, (1) and (2) were carried out in ethyl alcohol, (3) in toluene; (1) with a product obtained by steam distillation, (2) and (3) with the recrystallised product:

(1) 1.3718, made up to 19.95 c.c., gave  $\alpha +5.11$ , whence  $[\alpha]_D^{20} +37.08$ .

(2) 1.3719, made up to 19.85 c.c., gave  $\alpha +5.13$ , whence  $[\alpha]_D^{20} +37.03$ .

(3) 2.3056, made up to 20 c.c., gave  $\alpha +8.71$ , whence  $[\alpha]_D^{20} +37.77$ .

#### *d*- and *l*-isoborneol.

The commercial product (from camphene) supplied to the Schimmel and Co. was well crystallised, apparently homogeneous, and had a slight levorotation ( $[\alpha]_D^{20} -0.8^\circ$  in ethyl alcohol). It was readily converted into the hydrogen phthalic ester by heating with phthalic anhydride for eight hours at  $115-120^\circ$ . The *l*-isoborneyl hydrogen phthalate thus obtained crystallises in small clusters of prisms from glacial acetic acid, and melts at  $168^\circ$ .

*l*-Menthylamine *disoborneoyl Hydrogen Phthalate*.—The inactive (1 mol.) is dissolved in the calculated amount of a cold solution of sodium carbonate, and the solution precipitated with a cold solution of *l*-menthylamine hydrochloride (1 mol.). The resulting pasty mass soon hardens, and is then repeatedly crystallised in dilute alcohol. The first crop of crystals melts at  $105-106^\circ$ , and has  $[\alpha]_D^{20}$  about  $-6$  in ethyl alcohol ( $c=5.0$ ). The mother liquor from these is worked up as described below. The crystalline product after some seven or eight recrystallisations melts indefinitely at  $116-118^\circ$ , and has the specific rotation, which is unaltered by further recrystallisation,  $[\alpha]_D^{20} +29.29$  in ethyl alcohol ( $c=5$ ). The salt crystallises in clear, colourless, nodular clusters of prismatic needles; as the purification proceeds, however, the crystals, though of the same habit, become more dense and opaque. The

hydrolysed, and gave results in agreement with the formula:  $\text{H} \cdot \text{O}_2\text{C}_6\text{H}_4\text{CO}_2\text{H} \cdot \text{C}_{10}\text{H}_{13} \cdot \text{NH}_2$ .

*Isobornyl Hydrogen Phthalate*.—The menthylamine salt was dissolved in glacial acetic acid and poured into water, the precipitated ester being twice crystallised from glacial acetic acid. The product was thus obtained in small, rectangular prisms melting at  $71^\circ$ . A polarimetric observation gave the following result: 0.27, made up to 20 c.c. with chloroform, gave  $\alpha + 7.91^\circ$ , whence  $[\alpha]_D^{25} + 76.88^\circ$ .

*Isobornyl Isoborneol*.—The phthalate was heated for two hours on the water-bath with the calculated amount of alcoholic sodium hydroxide, and isoborneol separated from the solution by distillation with steam. Determination of the specific rotation of this product gave the following result:

0.28, made up to 20 c.c. with ethyl alcohol, gave  $\alpha + 3.48^\circ$ , whence  $[\alpha]_D^{25} + 34.02^\circ$ .

After recrystallisation from light petroleum, the rotation was unchanged:

0.51, made up to 19.9 c.c. with ethyl alcohol, gave  $\alpha + 3.75^\circ$ , whence  $[\alpha]_D^{25} + 34.08^\circ$ .

0.25, made up to 20 c.c. with ethyl alcohol, gave  $\alpha + 11.33^\circ$ , whence  $[\alpha]_D^{25} + 34.09^\circ$ .

The specific rotation in toluene solution was determined:

0.34, made up to 20 c.c. with toluene, gave  $\alpha + 1.91^\circ$ , whence  $[\alpha]_D^{25} + 21.32^\circ$ .

The melting point of the crystallised product was  $214^\circ$ , being  $4^\circ$  above the melting point of the product obtained from Schimmel.

*Camphor*, obtained from this by oxidation with nitrous fumes in chloroform solution, gave the following result in the polarimeter:

0.118, made up to 19.9 c.c. with ethyl alcohol, gave  $\alpha - 4.72^\circ$ , whence  $[\alpha]_D^{25} - 42.25^\circ$ .

The rotation of pure sublimed camphor at the same concentration was  $[\alpha]_D^{25} + 12.38^\circ$ .

The rotation of the *d*-isoborneol was unaltered by distillation with water, or in a strong solution of sodium hydroxide. Further proof of the purity of the product had not been racemised during the hydrolysis was obtained by reconvertng it into the hydrogen phthalate, which had  $[\alpha]_D^{25} + 76.4^\circ$ .

*Isobornyl Isobornyl Hydrogen Phthalate*.—The mother liquor from the first crop of crystals of the menthylamine salt (see p. 1978) was added to dilute acetic acid. The precipitated acid is then dissolved in alcohol and heated on the water-bath with the calculated

quantity of cinchonine.\* The base gradually dissolves, and, on cooling, the crude salt is deposited in hard, nodular crystals, which melt indefinitely at  $192\text{--}195^\circ$ , and have  $[\alpha]_D$  about  $+55^\circ$  in ethyl alcohol ( $c=5$ ). After five or six recrystallisations from alcohol, the salt has a constant rotation and melts at  $206^\circ$ :

0.3700 gave 16.6 c.c. moist nitrogen at  $20^\circ$  and 750 mm.  $N = 7.7$ .  
 $C_{19}H_{19}\cdot CO_2\cdot C_6H_4\cdot CO_2H\cdot C_{19}H_{22}ON_2$  requires  $N = 4.9$  per cent.  
 0.8762, made up to 20 c.c. with ethyl alcohol, gave  $\alpha = +55.1$ , whence  $[\alpha]_D = +43.25^\circ$ .

*l*-Isobornyl Hydrogen Phthalate.—The cinchonine salt is decomposed in an analogous manner to the *l*-menthylamine salt. The pure *l*-isobornyl hydrogen phthalate crystallises from glacial acetic acid in hard nodules and melts at  $167^\circ$ :

1.0100, made up to 20 c.c. with chloroform, gave  $\alpha = -7.77$ , whence  $[\alpha]_D = -76.93^\circ$ .

When hydrolysed by heating for two hours with alcoholic potassium hydroxide ( $2\frac{1}{2}$  mols.), it yields *isoborneol*, which was separated from the mixture by distillation with steam and gave the following result in the polarimeter:

0.7232, made up to 20 c.c. with ethyl alcohol, gave  $\alpha = -2.50$ , whence  $[\alpha]_D = -31.57^\circ$ .

After crystallisation from light petroleum, it melts at  $211^\circ$ . Determination of the specific rotation gave the following result:

1.0777, made up to 20 c.c. with ethyl alcohol, gave  $\alpha = -3.70$ , whence  $[\alpha]_D = -31.31^\circ$ .

*l*-Isobornyl *l*-menthylcarbamate,  $C_{10}H_{19}\cdot NH\cdot CO_2\cdot C_{19}H_{17}$ , was prepared by methods analogous to those described under borneol. The compound crystallised in beautiful, glistening, prismatic needles, which were recrystallised five times from dilute alcohol. The melting point of the product was indefinite, being about  $120^\circ$ , but the rotation remained practically unaltered, being  $[\alpha]_D = 55.8^\circ$  and  $[M]_D = 187$  in ethyl alcoholic solution with  $c=5$ ; thus indicating that no resolution had been effected. The two carbamates were, however, prepared from the *isoborneols* by heating with *l*-menthylcarbimide for twelve hours at  $120^\circ$ .

*l*-Isobornyl *l*-menthylcarbamate crystallises from alcohol in small prisms melting at  $128^\circ$ :

0.5293, made up to 19.85 c.c. with ethyl alcohol, gave  $\alpha = +55.8$ , whence  $[\alpha]_D = 1.41^\circ$ .

*l*-Isobornyl *l*-menthylcarbamate crystallises from dilute alcohol

\* Experiments were made with less than the calculated quantity of cinchonine, in a view to effecting a quicker resolution, but gave no more advantageous results.

prismatic needles melting at  $118^{\circ}$ , and is much more soluble in acidic media than the corresponding *dl*-compound :

0.76 g. made up to 20 c.c. with ethyl alcohol, gave  $\alpha = 5.91^{\circ}$ , whence  $[\alpha]_D^{20} = 112.0^{\circ}$ .

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#### XCIV.—*The Interaction of Metallic Sulphates and Caustic Alkalis.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

The immediate action of caustic alkalis on boiling solutions of sulphates of the heavy metals results, as is well known, in the precipitation of the metal as oxide or hydroxide, but it is only in a very few cases that any knowledge exists as to the product of the reaction at ordinary temperature, although a basic sulphate is generally thought to be formed, and many such basic sulphates have been isolated by various methods of procedure (see Habermann, *Monatsh.*, 1884, **5**, 112; Gugen, *Compt. rend.*, 1882, **94**, 1125; Pickering, *Trans.*, 1880, 1887; *Chem. News*, 1882, **45**, 121, and 1883, **47**, 181). For the purpose of an investigation to be described subsequently, it became necessary to ascertain the composition of these precipitates in the case of iron and copper, and the results thus obtained have been supplemented by an examination of the sulphates of other metals.

The examination was made by ascertaining the amount of alkali, usually either sodium or calcium hydroxide, required for the complete precipitation of the metal, and also the amount required to bring about an alkaline reaction, using phenolphthalein as indicator.

The precipitates are all of a bulky and flocculent nature, and the completion of the precipitation cannot be ascertained by allowing them to settle, and then adding more of the alkali: filtration is necessary, and the method which had to be adopted was to add various multiples of the alkali to similar quantities of the sulphate, and then by successive approximations the amount of alkali necessary for complete precipitation. In some cases, of course, this can be ascertained by the use of a more delicate test than the addition of metallic



Weak solutions were used in all cases, their strength being one gram-molecule in 100 litres.

The general character of the reaction appears to be similar with the metallic sulphates examined, and with all the caustic alkalis, metal is first precipitated as a basic sulphate of definite composition, which, on the addition of more alkali, is converted into a second, highly basic sulphate, before any alkaline reaction becomes evident in the liquid. In some cases, the transformation takes place in two distinct stages.

In every instance examined, the products of the reaction, so far as the basicity of the precipitates is concerned, are the same, whether lime or lime be used, but the precipitates are not always identical in respects, and this has been ascertained to be due to the fact that, when lime is used, they retain a considerable amount of the calcium sulphate formed in the reaction. The basicity of the products, however, alone be discussed at present.

#### *Copper Sulphate.*

The basic sulphates of copper were investigated by the author (1883 *Chem. News*, **47**, 181), and it was ascertained that two existed in definite form:  $3\text{CuO}\cdot\text{SO}_3$ , obtained by boiling a solution of copper sulphate, and  $4\text{CuO}\cdot\text{SO}_3$ , obtained (*a*) by precipitating copper sulphate solutions with an amount of potash not exceeding equivalent; (*b*) by decomposing the sulphate with an acetate, or by digesting copper hydroxide with a solution of the sulphate. The results were based on the analysis of the precipitates.

When an alkali is added gradually to a weak solution of copper sulphate, a point is reached when the liquid begins to show a distinct alkaline reaction, but this reaction is temporary, and more alkali must be added before a permanent alkalinity is obtained. The gradual absorption of alkali after the first temporary alkalinity occurs extends over two or three days. The equivalents of alkali required to produce the initial and permanent alkaline reaction, together with the equivalents required to precipitate the copper completely, were found to be:

	Complete precipitation.	Initial alkalinity.	Permanent alkalinity.
$\text{BaO}$ .....	—	0.993	0.993
$\text{CaO}$ .....	0.752	$\begin{cases} 0.864 \\ 0.877 \end{cases}$	$\begin{cases} 0.877 \\ 0.877 \end{cases}$
$\text{Na}_2\text{O}$ .....	0.766	$\begin{cases} 0.833 \\ 0.851 \end{cases}$	$\begin{cases} 0.841 \\ 0.851 \end{cases}$
$\text{Li}_2\text{O}$ .....	—	0.808	0.808
$\text{K}_2\text{O}$ .....	(0.75)	0.895	0.895
Mean .....	0.756	—	0.877

precipitation of the metal is complete when the alkali reaches equivalent, an amount showing that the basic sulphate then formed must have the formula  $4\text{CuO}\cdot\text{SO}_3$  (the value inserted for  $x$  is that given by the investigation of 1883). This sulphate is slowly converted into a more basic one by further addition of alkali, and permanent alkalinity is reached in all five cases when the alkali amounts to 0.9 equivalent. This represents the formation of  $10\text{CuO}\cdot\text{SO}_3$ . In only one instance, that of baryta, is the initial alkalinity identical with that of permanent alkalinity, a condition probably connected with the insolubility of barium sulphate. With lithia and potash, initial alkalinity occurs with 0.8 equivalent, but with soda and lime the values are higher. It seems probable, however, that in all cases the point of initial alkalinity indicates the existence of a basic sulphate intermediate between the initial and final products, although in some cases it may be impossible to find this intermediate compound unmixed with a certain amount of the final product, and hence the quantity of alkali absorbed is usually large. The initial alkalinity certainly marks a point at which there is a very great alteration in the rate at which the alkali is absorbed, an almost instantaneous absorption, changing to one of great slowness, although its rate varies with the alkali used. Moreover, the product obtained at the point of initial alkalinity is not intermediate in character between the highest and lowest sulphate, as if it were a mixture of these two. Taking the case of soda, the first product,  $4\text{CuO}\cdot\text{SO}_3$ , is a light, opaque, blue or greenish substance, which settles comparatively quickly in the liquid; the product,  $10\text{CuO}\cdot\text{SO}_3$ , is of a darker, full blue colour, less opaque, settles much more slowly; but the intermediate product, obtained when about 0.8 equivalent is added, is almost as dark as the compound  $10\text{CuO}\cdot\text{SO}_3$ , and is even more voluminous, settling very slowly in the liquid. To give an example: 1 gram of hydrated copper sulphate was precipitated by different amounts of lime water, so as to give the three basic sulphates in question, the total volume of the liquid in each case being 171 c.c.; after one hour, the precipitates weighed 83, 145 and 136 c.c. respectively, the second sulphate being not being intermediate in properties between the first and third. This was repeated many times, and always with the same results.

It is fairly certain, therefore, that in the case of the action of all alkalis (except baryta) on copper sulphate, an intermediate compound is formed, and it is probable, from the results with lithia and soda, that its formula is  $5\text{CuO}\cdot\text{SO}_3$ , corresponding to the addition of 0.5 equivalent of alkali.

It is necessary to add the alkali very slowly and cautiously to the

sulphate in order to obtain the first compound,  $4\text{CuO}\cdot\text{SO}_3$ , but a local excess of alkali tends to form some of the more basic sulphates, and then, more than 0.75 equivalent will be required to complete precipitation. In the same way, it requires great care to obtain the final sulphate,  $10\text{CuO}\cdot\text{SO}_3$ , without the production of any hydroxide in cases where such is produced by excess of alkali; where soda, lithia or potash is used, the precipitate then turns brown after a time. When precipitated with care, the basic sulphates themselves seem to be quite permanent in the liquids from which they are thrown down.

It was found that the final reaction with lime-water, the permanent alkalinity, was practically constant throughout the ordinary atmospheric temperatures, but that at higher temperatures the precipitate became less basic, attaining at  $100^\circ$  almost the composition of  $4\text{CuO}\cdot\text{SO}_3$ . The values obtained were:

At $5^\circ$ , 0.916 CuO required. $10\text{CuO}\cdot\text{SO}_3$ requires 0.916	
„ $25^\circ$ , 0.912 „ „ „ „ „ „	
„ $40^\circ$ , 0.825 „ „ „ „ „ „	
„ $70^\circ$ , 0.809 „ „ „ „ „ „	
„ $100^\circ$ , 0.764 „ „ „ „ „ „ $4\text{CuO}\cdot\text{SO}_3$ requires 0.75 CuO	

The results obtained when excess of lime-water is added to the sulphate are described in a subsequent communication (p. 1985).

#### *Iron Sulphates.*

With ferrous sulphate, the precipitation of the whole of the iron is coincident with the first appearance of an alkaline reaction, although duplicate determinations were not very concordant. Complete precipitation evidently occurs when a basic sulphate of the formula  $10\text{FeO}\cdot\text{SO}_3$  is formed, analogous to the final product in the case of copper sulphate. The values obtained were:

With Soda.	With Lime.
0.930 equiv.	0.868 equiv.
0.887 „	0.892 „
0.884 „	0.881 „
0.914 „	0.874 „
—	—
Mean 0.904 „	0.879 „

The temporary alkalinity disappears, and more alkali must be added before it becomes permanent, but the rate at which it disappears is less than in the case of copper sulphate, and the reaction is not complete for many days. It is difficult therefore to determine the point of completion with any degree of accuracy, but it evidently coincides with the removal of all the  $\text{SO}_3$  from the basic sulphate : the

the determinations with soda gave  $1.029 \text{ Na}_2\text{O}$  as having been added; five determinations with lime gave  $1.013 \text{ CaO}$ . With ferric sulphate, the complete precipitation of the metal and the appearance of alkalinity were coincident, the equivalents of alkali added being  $3 \times 0.772$  in the case of soda, and  $3 \times 0.817$  (mean of  $0.803$ ) in the case of lime. The further absorption of alkali was in other cases, but with such slowness that it is almost impossible to determine the final point: using soda, this point would be  $3 \times 0.860$  equivalents. None of these values is exactly concordant or exact to justify the assigning of any formula to the basic sulphates formed; all that is certain is that a basic sulphate is formed, and that it is then converted by further alkali into a more highly basic one.

The investigation of the basic ferric sulphates was published by the author (Trans., 1880, 37, 807); the investigation was on lines different from those followed here, and, of the many basic sulphates said to exist, evidence in favour of one only was found, namely,  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{SO}_4$ ; this sulphate would correspond with a reaction requiring addition of  $3 \times 0.833$  equivalents of alkali; the determinations just given give values neighbouring on this quantity, and, no doubt, this is the sulphate figures in the precipitation of ferric sulphate by alkalis.

#### *Nickel Sulphate.*

With soda, the whole of the metal was precipitated when the alkali added was  $0.422$  equivalent, and the liquid then showed a barely perceptible alkaline reaction. With lime-water, a similar result was obtained, the value found being  $0.401$  equivalent. This indicates the formation of  $5\text{NiO} \cdot 3\text{SO}_3$ . When more of either of these alkalis was added, no further increase in alkalinity occurred until the total added was either  $0.6$  or  $0.8$  of an equivalent. Whether the one or the other of these two proportions marks the point at which a definite change in the pink colour of the phenolphthalein is noticed seems to depend somewhat on the conditions under which the reaction occurs, such as the dilution of the liquid, and the rate at which the alkali is added. Both stages may sometimes be noticed in the same experiment, but the bulk of substance dealt with, and the conditions under which the observation of changes of colour, are suitable.

The values obtained on various occasions were:

With soda	0.598	With soda	0.812
" lime	0.582	" lime	0.803
" "	0.596	" "	0.810
Mean	0.592		0.808

These indicate the existence of  $5\text{NiO}, 2\text{SO}_3$  and  $5\text{NiO}, \text{SO}_3$ , in which are, no doubt, formed in succession from the primary duct,  $5\text{NiO}, 3\text{SO}_3$ . The last change, to  $5\text{NiO}, \text{SO}_3$ , is the one which is most marked.

#### *Cobalt Sulphate.*

With cobalt sulphate, the results are different from those with nickel sulphate, for a permanent alkaline reaction appears as soon as the precipitation of the metal is complete. This occurs when soda amounts to 0.759 equivalent, or three-quarters of that required for total decomposition, representing therefore the formation of  $\text{HCoO}_2\text{SO}_3$ .

There is, apparently, a preliminary action in the case of cobalt, in the case of the other sulphates. A faint alkaline reaction appears when the alkali added amounts to about 0.3 equivalent, but further additions of alkali cause no corresponding increase in alkalinity until, as has been said, the amount added reaches one equivalent. This preliminary stage, however, does not seem to indicate the composition of the basic sulphate present, as part of the metal is still in solution.

The precipitate formed during this first stage is green, but on adding more alkali it becomes blue.

#### *Manganese Sulphate.*

The whole of the metal in this case was not precipitated by soda until the latter amounted to 1.019 equivalents. There is hence, therefore, no indication of any basic sulphate being formed. Therefore, with lime was not examined.

#### *Zinc Sulphate.*

With zinc sulphate and soda, the complete precipitation of the metal was coincident with the appearance of a permanent alkaline reaction, and no preliminary or secondary reaction was noticed. The alkali required was found to be 0.795 equivalent, indicating, therefore, the composition of the precipitate to be  $5\text{ZnO}, \text{SO}_3$ .

#### *Cadmium Sulphate.*

With cadmium sulphate a slight pink colour was noticed (pyrophthalic acid being present) on the addition of only a small amount of soda, but it is the precipitate, and not the liquid, that becomes coloured; the latter shows no alkaline reaction until the whole of

precipitated. This occurs when the alkali amounts to 0.731 equivalent, indicating, although not very exactly, the formation of a sulphate of the composition  $4\text{CdO}, \text{SO}_3$ .

#### *Magnesium Sulphate.*

With magnesium sulphate, soda completed the precipitation when added to 1.034 equivalents. No basic sulphate therefore seems to be formed in this case.

#### *Aluminium Sulphate.*

The addition of soda to aluminium sulphate completes the precipitation when the quantity added reaches  $3 \times 0.611$  equivalents, which implies that the basic sulphate formed is  $5\text{Al}_2\text{O}_3, 6\text{SO}_3$ . The excess in the soda over that calculated is accounted for by a interchange, similar to that observed in other cases, since the precipitate is converted into a more basic sulphate by a further addition of alkali, the alkaline reaction not becoming permanent until the total alkali amounts to  $3 \times 0.95$  molecules. With lime-water, a similar precipitation gave  $3 \times 0.970$  molecules as requisite. The secondary reaction was a very slow one, requiring several days, and, possibly, was not quite complete even then, so that in all probability the final product is alumina containing no  $\text{SO}_3$ .

As many as nine basic sulphates of aluminium have been stated by French chemists to have been obtained; but an examination undertaken by the present author in 1882 (*Chem. News*, 45, 121) threw considerable doubt on the existence of all of them as definite compounds. The list of these did not contain the one now indicated.

#### *Summary.*

Alkalis added to solutions of the metallic sulphates here examined precipitate a definite basic sulphate, except in the case of manganese sulphate, where the hydroxide is precipitated. After the precipitation is complete, the further addition of alkali converts the basic sulphate into another, sometimes consecutively into two other, products (for example, copper, nickel), or into the hydroxide (aluminium). When one of the stronger alkalis (potash, soda) is in excess, the product is probably always the hydroxide, but, in the case of lime, this does not appear to be so, at any rate not with sulphates of copper and nickel, as will be shown in the following section. In every case examined, different alkalis have given the same results as regards the basicity of the sulphates precipitated from each particular case. The existence of the following eleven

basic sulphates has been established in this way: the predominance of five as the coefficient of equivalents of metallic oxide present is noticeable. Those marked with an asterisk are the ones formed; the whole of the metal has been precipitated from the solution; the others are products of the action of further quantities of alkali:

$5\text{NiO}, 3\text{SO}_4^*$ ,  $5\text{NiO}, 2\text{SO}_3$ ,  $5\text{Al}_2\text{O}_3, 3 \times 2\text{SO}_3^*$ ,  $4\text{CuO}, \text{SO}_3^*$ ,  $4\text{CuO}, 3\text{SO}_3^*$ ,  $4\text{CoO}, \text{SO}_3^*$ ,  $5\text{CuO}, \text{SO}_3$ ,  $5\text{NiO}, \text{SO}_3$ ,  $5\text{ZnO}, \text{SO}_3^*$ ,  $10\text{CuO}, \text{SO}_3$ ,  $10\text{FeO}, \text{SO}_3$ .

The basic sulphates obtained by Habermann (*loc. cit.*), by adding ammonia to boiling solutions of the sulphates, differ from those above, the compounds described by him being  $7\text{CuO}, \text{SO}_3$ ,  $7\text{NiO}, \text{SO}_3$ ,  $5\text{CoO}, \text{SO}_3$ ,  $4\text{ZnO}, \text{SO}_3$ , and  $2\text{CuO}, \text{SO}_3$ . Gorgeu also gives  $3\text{NiO}, 2\text{SO}_3$ , and Schindler,  $2\text{ZnO}, \text{SO}_3$ ; the literature of the sulphates of copper, iron and aluminium will be found in the communications by the present author referred to above.

## CXCV.—The Chemistry of Bordeaux Mixture

By SPENCER UMERVILLE PICKERING, M.A., F.R.S.

BORDEAUX mixture, or *bouillie bordelaise*, has been in use as a fungicide since 1883. The discovery of its value was accidental. It had been the practice in the vineyards in the neighbourhood of Bordeaux to sprinkle those vines which were infested with veridigris, in order to give them the appearance of having been poisoned, and so to prevent depredations. A mixture of lime and copper sulphate was soon substituted for the verdigris, cheaper, and, when the downy mildew of America (*Powdery mildew*) made its appearance in Europe, it was noticed (1892) that those vines which had received the copper dressing were those which kept their leaves longest, and were least affected by the mildew.

The mixture in general use at present is made by mixing 1 part by weight of lime, made into a milk, to 1·6 parts of eight-hydrate copper sulphate dissolved in 100 parts of water. This is known in America as the "normal" or "1·6" mixture. Occasionally stronger or weaker mixtures are used, and sometimes the proportion of lime added is increased so as to be equal to that of the sulphate. For complete decomposition, the crystallised sulphate would require one-fifth of its weight of pure lime; therefore the lime used in practice is always in considerable excess, even when liberal allowance is made for impurities in it.

It is somewhat remarkable that the nature of the sulphate is

that this mixture has not yet been elucidated. The reaction is generally represented as resulting in the formation of cuprous hydroxide, although occasionally it is suggested that a basic cuprous sulphate may be formed, and an equation is given representing a cuprous sulphate ( $2\text{CuO} \cdot \text{SO}_3$ ) which, so far as is known, has no existence. That copper hydroxide is the product of the reaction is not a subject of serious consideration, for this hydroxide, as is well known, loses its water and its blue colour in a very short time, becoming black, whereas Bordeaux mixture remains quite blue for a considerable period. It is true that caustic potash in excess of that required to form basic sulphate of copper results in the formation of cuprous copper hydroxide, and that in Bordeaux mixture the alkali is in considerable excess; but it does not by any means follow that cuprous hydroxide will behave in the same manner as excess of potash. The action of lime on copper sulphate is somewhat variable, and the reaction, as complicated, would appear to be probable from the considerable variations which are noticed in the blue colour of the precipitate obtained in preparing Bordeaux mixture. These variations may sometimes be explained by differences in the colour of the lime used, but they are due, as will be seen, to the fact that there are formed, under different conditions, substances with considerable differences of colour. Occasionally the precipitate will be found to be violet, and even to purple: this coloration is probably accidental, and is due to the presence of some pink compound formed by organic matters exhibiting the biuret reaction. On several occasions, when dealing with emulsions of petroleum with basic copper sulphate, streaks of a pink compound have been noticed in the blue precipitate.

If Bordeaux mixture made with milk of lime, there must be free lime, and, generally, calcium carbonate, mechanically mixed with the precipitate, and any direct investigation of the composition of the precipitate would be of little value. Lime water, therefore, is not used instead of milk of lime; but, even then, any analysis of the precipitate was practically impossible, for it is very bulky and difficult to wash, whilst water, as will be shown, partly decomposes it, and it does carbon dioxide. The method of examination adopted, therefore, was to mix known weights of copper sulphate with known solution, and to deduce the composition of the precipitate formed by determining what was left dissolved in the solution. This is either calcium sulphate only, or calcium sulphate and cuprous sulphate where an excess of lime has been used; the latter was determined by titration, and the former, either as barium sulphate, or by precipitation to dryness and igniting. In some cases, the precipitation was effected in the presence of excess of sodium sulphate,



and then the mixed sulphates left in solution had to be determined by a separate determination of the amount of calcium in them.

As has been shown in the previous communication (p. 188), precipitation of the copper is complete when enough lime is added to form the basic sulphate  $4\text{CuO}\cdot\text{SO}_3$ , and this sulphate is decomposed on further addition of alkali until the compound  $\text{CuO}\cdot\text{SO}_3$  is formed: in addition to these, a sulphate of an intermediate composition, probably  $5\text{CuO}\cdot\text{SO}_3$ , is also produced.

Although, as regards basicity, the precipitates formed by different alkalis are used are identical, a qualitative examination is sufficient to show that they are not identical in other respects. Thus, on precipitating copper sulphate with sufficient alkali to form  $5\text{CuO}\cdot\text{SO}_3$ , the volume of the liquids being the same, the precipitate with lime is found to be of a pale blue, whereas that with soda is very much darker; the former, also, is either finer-grained or more dense than the latter, for, even after being allowed twenty-four hours to settle, it occupies a volume half as great again as that of the precipitate given by lithia resembles that with lime, and is paler in colour and more bulky, whereas that given by potash resembles the soda precipitate, except that it is slightly more bulky. Similar differences in appearance are noticed if the precipitates consisting of  $4\text{CuO}\cdot\text{SO}_3$ , obtained by different alkalis, are compared. The more minute state of division of the lime precipitates, contrasted with those given by soda, is further illustrated by the greater emulsifying powers of the former, which will be dealt with in a subsequent communication. With the basic ferrous sulphate it may be mentioned, a like difference of behaviour characterises the precipitates thrown down by different alkalis.

These differences, however, are not of a physical character, for the two precipitates behave differently when treated with excess of the same alkali: the soda precipitate, when treated with a further equivalent of caustic potash, begins to blacken in a few hours; with a further equivalent of soda it begins to blacken in a few hours; and with an equivalent of lime, blackening commences after about six weeks; with the lime precipitate, however, blackening is produced by excess of soda only after two or three weeks, whereas excess of neither potash nor lime seem to have any effect on it.

Passing to the quantitative examination, Table I contains the values given when copper sulphate is precipitated with varying proportions of lime. The molecular proportions of the reagents taken are entered in the first two columns, and the molecular composition of the precipitate, as given by the analysis of the liquid solution, in the third. The solution of copper sulphate

TABLE I.—*Precipitation of Copper Sulphate by Lime-Water.*

Proportions taken.		Composition of precipitate.
CuSO <sub>4</sub> .	CaO.	
10	7.5	10CuO, 27.5SO <sub>3</sub> , 0.2 CaSO <sub>4</sub>
10	8	10CuO, 28SO <sub>3</sub> , 0.75CaSO <sub>4</sub>
10	8	10CuO, 28SO <sub>3</sub> , 0.66CaSO <sub>4</sub>
10	9	10CuO, 28SO <sub>3</sub> , 1.45CaSO <sub>4</sub>
10	9	10CuO, 28SO <sub>3</sub> , 1.31CaSO <sub>4</sub>
10	9	10CuO, 28SO <sub>3</sub> , 1.25CaSO <sub>4</sub>
10	18	10CuO, SO <sub>3</sub> , 1.42CaSO <sub>4</sub> , 2.66CaO
10	18	10CuO, SO <sub>3</sub> , 0.88CaSO <sub>4</sub> , 3.06CaO
10	27	10CuO, SO <sub>3</sub> , 1.11CaSO <sub>4</sub> , 3.06CaO
10	27	10CuO, SO <sub>3</sub> , 1.11CaSO <sub>4</sub> , 2.75CaO
10	36	10CuO, SO <sub>3</sub> , 0.84CaSO <sub>4</sub> , 3.11CaO
	<i>Mean</i> .....	<i>10CuO, SO<sub>3</sub>, 1.01CaSO<sub>4</sub>, 2.91CaO</i>
10	54	10CuO, SO <sub>3</sub> , 1.38CaSO <sub>4</sub> , 2.11CaO
10	198	10CuO, SO <sub>3</sub> , 0.98CaSO <sub>4</sub> , 7.21CaO
10	150	10CuO, 0.47SO <sub>3</sub> , 15.7CaO
10	210	10CuO, 18.6CaO
10	390	10CuO, 20.6CaO
10	490	10CuO, 28.1CaO
10	1020	10CuO, 32.6CaO
10	1810	10CuO, 28.5CaO
10	5100	10CuO, 31.1CaO
	<i>Mean</i> .....	<i>10CuO, 29.1CaO</i>

and 10 per cent. of CuSO<sub>4</sub>.5H<sub>2</sub>O, and the lime water contained 0.135 per cent. of CaO; in the case where the smallest amount of lime-water was used, the mixture would be of about the strength of normal Bordeaux mixture. The proportions in the table are all expressed so as to refer to 10CuO.

In the first six experiments, the lime added was only just sufficient to form one or other of the three definite basic sulphates, but in all cases, as will be seen, these contain a certain amount of precipitate. With 4CuO.SO<sub>3</sub> (Nos. 1), the amount is very small; with 5CuO.SO<sub>3</sub> (Nos. 2 and 3) it is much greater (although not considerably in the duplicate determinations), and with 6CuO.SO<sub>3</sub> (Nos. 4-6) it is greater still, there being then more calcium as calcium sulphate than in the basic copper sulphate. Taking into consideration the large and approximately equal proportion of calcium sulphate in the latter case, and the fact that the amount here present is very different from what it is in the less basic sulphates, the conclusion is that the calcium must be present as a chemical constituent of the molecule. The values, however, are not sufficiently near to a simple fraction to lead to a definite formula for the complex sulphate.

No doubt, all these precipitates are unstable compounds, the composition of which would be affected by such circumstances as temperature and strength of the solution; indeed, they react with up some of their calcium sulphate to water. This was especially followed: the mixture in No. 6 was filtered, and the precipitate measured and analysed; the measurement showed what volume of liquid was retained by the precipitate on the filter; the precipitate with this liquid was then mixed with water equal in volume to that originally present, and the amount of sulphate passing in solution was determined. This was found to be greater than that in the liquid adhering to the precipitate, so that some calcium sulphate must have been derived from the precipitate in the solution. The precipitate, which originally contained  $1.25\text{CaSO}_4$ , contained only  $1.04\text{CaSO}_4$ . A similar experiment with the less soluble precipitate in No. 3 gave similar results, the  $0.46\text{CaSO}_4$  originally present being reduced to  $0.35\text{CaSO}_4$ .

The circumstances conditioning the amount of calcium sulphate in these basic sulphates were examined in other experiments which may be described before dealing with the further results in Table I.

Table II contains results in which the precipitation was effected in the presence of excess of calcium sulphate. In Nos. 23, 27 and 28 the calcium sulphate added was equivalent to 1, 2 and 3

TABLE II.—*Precipitation of Copper Sulphate by Lime-Water with Excess of Calcium Sulphate Present.*

No.	Proportions taken.		Composition of precipitate.
	$\text{CuSO}_4$	$\text{CaSO}_4$	
	$10\text{CuO}, \text{SO}_3$ formed.		
(10).....	10	7.5	$10\text{CuO}, 2.75\text{SO}_3$
(11).....	10	7.5	$10\text{CuO}, 2.75\text{SO}_3$
(12).....	10	7.5 Saturated	$10\text{CuO}, 2.75\text{SO}_3$
	$5\text{CuO}, \text{SO}_3$ formed.		
(23).....	10	8	$10\text{CuO}, 2\text{SO}_3$
(24).....	10	8	$10\text{CuO}, 2\text{SO}_3$
(25).....	10	8	$10\text{CuO}, 2\text{SO}_3$
(26).....	10	8 Saturated	$10\text{CuO}, 2\text{SO}_3$
	$10\text{CuO}, \text{SO}_3$ formed.		
(27).....	10	9	$10\text{CuO}, \text{SO}_3$
(28).....	10	9	$10\text{CuO}, \text{SO}_3$
(29).....	10	9	$10\text{CuO}, \text{SO}_3$
(30).....	10	9	$10\text{CuO}, \text{SO}_3$
(31).....	10	9	$10\text{CuO}, \text{SO}_3$
(32).....	10	9	$10\text{CuO}, \text{SO}_3$
(33).....	10	9 Saturated	$10\text{CuO}, \text{SO}_3$

two, two and three times respectively, that formed in the first experiment. The excess of lime-water neutralised with sulphuric acid before

for the purpose; but the water present was increased in similar proportions, so that the strength of the solution as regards its calcium sulphate contents was the same in all cases. All these solutions, however, were supersaturated with calcium sulphate, for 100 parts of water at 15° dissolve 0.129 gram of lime, but only 0.197 gram of calcium sulphate (equivalent to 0.081 gram  $\text{CaO}$ ), so that the amount available for combining with the basic sulphate would be increased by increasing the amount of calcium sulphate solution. It was, however, found that no such increase of sulphate in the precipitate is obtained thereby.

A supersaturated solution of calcium sulphate obtained by saturating lime-water with sulphuric acid remains very persistently supersaturated, and no trace of sulphate is deposited for at least twenty-eight hours; it is improbable therefore that these precipitates were contaminated with calcium sulphate which had been precipitated out, as they were all filtered from the liquid after twenty-four hours of being precipitated. To obviate such a possibility, however, the experiments were repeated in the presence of a large weighed crystal of selenite, on to which any calcium sulphate would be deposited from the liquid, whilst, at the same time, the liquid would be kept saturated. The mixtures were left for nine weeks before analysis (which included the determination of the increase in weight of the selenite crystals); the results (Nos. 22, 25 and 28) give substantially the same values as the other experiments for the composition of the precipitates. It should be mentioned, however, that one series made at a lower temperature gave higher values in the case of all three basic sulphates for the amount of calcium sulphate present; this series has not been included here, as there was another circumstance connected with it which prevented its being strictly comparable with the others.

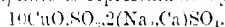
Of the three basic sulphates,  $10\text{CuO} \cdot \text{SO}_3$  is the one in which the calcium sulphate contents show least variation. The mean of the six determinations gives the approximate formula for this precipitate as  $10\text{CuO} \cdot \text{SO}_3 \cdot 1.28\text{CaSO}_4$ ; the means for the other basic sulphates are  $10\text{CuO} \cdot 2.8\text{SO}_3 \cdot 0.47\text{CaSO}_4$  and  $10\text{CuO} \cdot 2.5\text{SO}_3 \cdot 0.16\text{CaSO}_4$ . These results are connected with an investigation which will be published later, it was necessary to ascertain whether the composition of these basic copper sulphates was modified by the presence of sodium sulphate in the solution. With this object in view, known quantities of sodium sulphate were added to the copper solution before the addition of the lime. The results are given in Table III. With the basic sulphate  $10\text{CuO} \cdot \text{SO}_3$ , the small amount of calcium sulphate present in it is entirely ousted, and its place

TABLE III.—*Precipitation of Copper Sulphate by Lime-Water, Sodium Sulphate Present.*

	Proportions taken.			Composition of precipitate.
	CuSO <sub>4</sub>	CaO	Na <sub>2</sub> SO <sub>4</sub>	
		(a).	4CuO.SO <sub>3</sub> formed.	
(1) .....	16	7.5	0	10CuO, 2.5 SO <sub>3</sub> , 0.2 CaSO <sub>4</sub>
(2) .....	10	7.5	30	10CuO, 2.55SO <sub>3</sub> , 0.75Na <sub>2</sub> SO <sub>4</sub>
		(b).	5CuO.SO <sub>3</sub> formed.	
(3) .....	16	8	0	10CuO, 2SO <sub>3</sub> , 0.62CaSO <sub>4</sub>
(4) .....	10	8	30	10CuO, 2.02SO <sub>3</sub> , 0.34CaSO <sub>4</sub> , 0.38Na <sub>2</sub> SO <sub>4</sub>
		(c).	10CuO.SO <sub>3</sub> formed.	
(5) .....	16	9	0	10CuO, 1.8SO <sub>3</sub> , 1.35CaSO <sub>4</sub>
(31) .....	10	9	15	10CuO, 1.95SO <sub>3</sub> , 1.63CaSO <sub>4</sub> , 0.42Na <sub>2</sub> SO <sub>4</sub>
(32) .....	10	9	30	10CuO, 1.69SO <sub>3</sub> , 1.21CaSO <sub>4</sub> , 0.42Na <sub>2</sub> SO <sub>4</sub>
(33) .....	10	9	45	10CuO, 1.61SO <sub>3</sub> , 0.99CaSO <sub>4</sub> , 1.41Na <sub>2</sub> SO <sub>4</sub>
(34) .....	10	9	45	10CuO, 1.72SO <sub>3</sub> , 0.77CaSO <sub>4</sub> , 1.45Na <sub>2</sub> SO <sub>4</sub>
Mean of 21 to 27 .....				10CuO, 1.64SO <sub>3</sub> , 1.00CaSO <sub>4</sub> , 1.41Na <sub>2</sub> SO <sub>4</sub>

is taken by a proportionately large amount of sodium sulphate, a similar change occurs with both the other basic sulphates, and the displacement of the calcium sulphate is not completed; 5CuO.SO<sub>3</sub> about half the calcium sulphate is removed, and 10CuO.SO<sub>3</sub> about two-thirds; whilst in all cases the amount of sodium sulphate in the precipitate is greater than that of calcium sulphate which it displaces.

The four determinations with the most basic sulphate all indicate a definiteness in composition, for the sum of molecular proportions of sodium and calcium sulphates present is constant in spite of the variations in the proportions of sodium sulphate taken, and the precipitate is representable by the formula



In only one of the determinations (33) are the values at variance with this formula, but the experimental errors are considerable, for the amount of SO<sub>3</sub> in the precipitate is determined from the difference between quantities of ten to twenty per cent. magnitude, and the lime to be determined is present in very small amount. It is probable, indeed, that the molecular proportions of calcium and sodium sulphate are constant throughout, and of being merely interchangeable, and the mean of the results will be seen, gives almost exactly equal molecular proportions to these two.

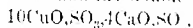
It will be noticed that the SO<sub>3</sub> united with the copper oxide in these cases, represented by an exact number of equivalents

Thus, the values given are dependent on the analysis, being the difference between the total  $\text{SO}_3$  in the precipitate and that precipitated with the lime and soda present, instead of being deduced, as in the other cases, from the amount of lime-water neutralised.

With the two less basic sulphates, the experiments were not sufficient so as to determine the exact formula of the precipitates; it is probable, however, that with the second sulphate the formula corresponds to  $10\text{CuO}, 2\text{SO}_3, (\text{Na}, \text{Ca})\text{SO}_4$ , that is, a compound containing only half as much of the neutral sulphates as is present in the most basic sulphate. In all three cases the proportion of total  $\text{CuO}$  to  $\text{CaO}$  in the molecule seems to be nearly constant, and approximates 3:10; the less there is present in combination with copper the more there is present as sulphate of calcium or soda.

Turning now to Table I, the experiments in the lower portion refer to cases where lime is added in excess. The results are also remarkable. With all proportions of lime between 10 to 100  $\text{CaO}$  to each  $10\text{CuO}$  (Nos. 7 to 11) the same compound is formed, this being the basic copper sulphate combined with one molecule of calcium sulphate and three of calcium oxide, or, in other words, a double basic sulphate of copper and calcium of the formula  $10\text{CuO}, \text{SO}_3, 4\text{CaO}, \text{SO}_3$ . When the proportion of lime taken increased beyond 40  $\text{CaO}$  to each  $10\text{CuO}$ , the precipitate rapidly becomes more basic, and with proportions exceeding 100  $\text{CaO}$  the precipitate begins to disappear, until, with still greater excess of lime, we get a precipitate which is a double oxide of copper and calcium. This attains to a constant composition when the proportion of lime reaches about 500  $\text{CaO}$  to  $10\text{CuO}$ , and continues up to the end of the series, where 5100  $\text{CaO}$  to  $10\text{CuO}$  is taken. The composition of this double oxide is  $\text{CuO}, 3\text{CaO}$ ; mean of the last four determinations giving  $\text{CuO}, 3.01\text{CaO}$ .

Between the double oxide and the double basic sulphate

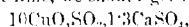


is probably another definite compound formed, and, as the double sulphates of calcium and of copper appear to be  $(\text{M}^{\text{O}}, \text{SO}_3)_2$ , we may conjecture that the higher ones are  $(\text{M}^{\text{O}}, \text{SO}_3)_3$ , and that the highest double basic sulphate has the formula  $10\text{CuO}, \text{SO}_3, 10\text{CaO}, \text{SO}_3$ . The values found in No. 13 are close to this, being  $10\text{CuO}, \text{SO}_3, 8.2\text{CaO}, \text{SO}_3$ , but it would require several determinations with amounts of lime intermediate between those in Nos. 13 and 14 to settle whether the limit here reached is really reached before the  $\text{SO}_3$  begins to be abstracted from the molecule.

The existence of this second double basic sulphate is emphasised

when the results are plotted out. Plotting the lime in the precipitate against the amount of lime taken (it is best to take the logarithms of these quantities), it is clear that the values for the precipitates contain  $\text{CaSO}_4$  are not continuous with those where they contain none; the experiments 11 to 13 lie on one straight line, and 14 to 17 on another, there being some considerable gap between 13 and 14. The rest of the figure is made up of three horizontal lines, the first representing the results of Nos. 1 to 10, where there is no lime in the precipitate, and the second representing the results of Nos. 7 to 11, where the double basic sulphate is formed, and the third, the results of Nos. 17 to 20, when the oxide has attained constancy of composition.

In Bordeaux mixture, the highest proportion of lime used is five equivalents to each equivalent of copper sulphate, that is, equal weights of the two; this is about the proportion in experiment 12 in Table I, but, as the lime is always far from pure, the actual proportions of calcium oxide would be smaller. The reaction occurring would rarely go beyond the stage reached in experiments 7 to 11, that is,  $10\text{CuO} \cdot \text{SO}_3 \cdot 4\text{CaO} \cdot \text{SO}_3$  would be the compound formed. With still smaller proportions of lime, or impure and carbonated lime, we should get the compound



or even a less basic sulphate down to  $4\text{CuO} \cdot \text{SO}_3$ . The early appearance of these products would account for the difference observed in the appearance of Bordeaux mixture, the basic sulphates,  $4\text{CuO} \cdot \text{SO}_3$  and  $10\text{CuO} \cdot \text{SO}_3 \cdot 4\text{CaO} \cdot \text{SO}_3$ , being much paler in colour than the intermediate sulphates.

When Bordeaux mixture is applied to trees, it liberates, at first, small quantities of copper sulphate, and it is to this, not to the copper that its fungicidal action is attributable. The reaction, doubtless, consists of  $x\text{CuO} \cdot y\text{SO}_3 + (x-y)\text{CO}_2 = (x-y)\text{CuCO}_3 + y\text{SO}_2$ .

One of the disadvantages attending its use, however, is that a certain time elapses before the fungicidal action comes into play. The nature of the compound of which Bordeaux mixture has been found to consist, will explain the occurrence of this delay. With a basic sulphate of copper and calcium, the basic sulphate of copper would probably not be attacked by the carbon dioxide, but all the basic sulphate of calcium in it had been decomposed. If this is the case, was verified by suspending in equal bulks of various basic sulphates containing the same amount of copper, and passing the same slow stream of carbon dioxide through them, and testing these at intervals to ascertain how long it took to liberate recognisable quantities of copper passed into solution. The results were as follows:—

... 10CuO, 2.28SO <sub>3</sub> , 0.16CaSO <sub>4</sub> .....	3-5 minutes
... 10CuO, 28SO <sub>3</sub> , 9.47CaSO <sub>4</sub> .....	10 "
... 10CuO, 80 <sub>3</sub> , 1.28CaSO <sub>4</sub> .....	10 "
... 10CuO, 80 <sub>3</sub> , 4CaSO <sub>4</sub> .....	45 "

length of the interval in the case of the last compound, as compared with that in the case of the others, is very noticeable. The quantity of lime had, of course, to be added to precipitate the last compound, but that was removed by filtration before the precipitate was mixed with the carbon dioxide; when it was not removed (and this is the case with Bordeaux mixture in practice) a still longer interval, namely, seventy-five minutes, elapsed before copper was precipitated. The longer interval in the case of the second and third compounds, as compared with the first, is, of course, due to the smaller amounts of copper sulphate which they are able to liberate. The delay in the action of the fungicide would, therefore, be remedied by using only sufficient lime to produce the basic sulphate 10CuO, 8SO<sub>3</sub>, instead of the double basic sulphate 10CuO, 8SO<sub>3</sub>, 10CaO, SO<sub>4</sub>; there would also be a considerable economical advantage in doing so, since the fungicidal value depends on the amount of normal copper sulphate eventually liberated, and the basic sulphate 10CuO, 8SO<sub>3</sub> will liberate two and a half times as much of the normal compound as will 10CuO, 28SO<sub>3</sub>, calculated on the same weights of copper sulphate used in preparing them. If, on the other hand, the proportion of lime used were increased to about five times that of copper sulphate (actual weights), the insecticidal value would be entirely destroyed, for the product then would consist of the basic oxide, without any SO<sub>3</sub> in it.

To make the basic sulphate 10CuO, 8SO<sub>3</sub>, it is necessary to use milk of lime instead of milk of lime, and this would be a further disadvantage from several other points of view, for the presence of the alkali clogs and wears the spraying nozzles, and entails loss of copper owing to its being easily knocked off the leaves.

Copper, by weight of crystallised copper sulphate requires about 100 parts of lime-water for its precipitation (the completion of which may of course, always be verified by testing with ferrocyanide); an increase in the proportion of lime would result in a diminution of the fungicidal value; thus, an increase to 143 c.c. would be sufficient for the precipitation of 10CuO, 28SO<sub>3</sub>, 7CaSO<sub>4</sub>, and a consequent reduction of the efficacy by one-fifth.

A Bordeaux mixture made as here suggested would be rather more economical than the "normal" mixture, although it would contain only about half the amount of copper, and would also cost less.

\* A solution containing 6.992 per cent. of CuSO<sub>4</sub>, 5H<sub>2</sub>O gives a visible coloration to a solution of ferrocyanide.



than half. Of course, the volume of lime-water required may vary somewhat with the temperature, but the variation in the basicity of lime throughout the range of ordinary atmospheric temperatures is small, being given as 0.137 part in 100 parts of water at 5°, and 0.125 part at 20°. According to these values, 130 c.c. would be required at 5°, and 123 c.c. at 20°, to precipitate the copper in one gram of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The figures agree almost exactly with the amount (134 c.c.) which has been found necessary in practice when working either at winter or summer temperatures.

A few experiments were made using caustic soda (free from carbonate) instead of lime-water. The results are given in Table IV.

TABLE IV.—*Precipitation of Copper Sulphate by Caustic Soda*

	Proportions taken.			Composition of precipitate.
	$\text{CuSO}_4$	$\text{Na}_2\text{O}$	$\text{Na}_2\text{SO}_4$	
25 .....	10	7.5	--	$10\text{CuO} \cdot 2.5\text{SO}_3 \cdot 0.01\text{Na}_2\text{SO}_4$
65 .....	10	8	--	$10\text{CuO} \cdot 2\text{SO}_3$ (no $\text{Na}_2\text{SO}_4$ )
37 .....	10	9	--	$10\text{CuO} \cdot \text{SO}_3 \cdot 0.06\text{Na}_2\text{SO}_4$
(25) .....	10	9	15	$10\text{CuO} \cdot \text{SO}_3 \cdot 0.5\text{Na}_2\text{SO}_4$
39 .....	10	9	45	$10\text{CuO} \cdot \text{SO}_3 \cdot 1.33\text{Na}_2\text{SO}_4$

When the basic sulphates formed are  $4\text{CuO} \cdot \text{SO}_3$ , or  $5\text{CuO} \cdot \text{SO}_3$ , there is no sodium sulphate combined with them, and when  $10\text{CuO} \cdot \text{SO}_3$  is the product, the amount is so small that it is always within the limits of experimental error, namely,  $0.06\text{Na}_2\text{SO}_4$ . When an excess of sodium sulphate is present, however, the amount of the precipitate is increased, but the experiments were not extensive enough to show what ultimate limits are attained. The absence of any sodium sulphate in the precipitate consisting of the less basic sulphates is in harmony with a similar observation made in 1883 (*Chem. News*, **47**, 182) as regards  $4\text{CuO} \cdot \text{SO}_3$  when precipitated by potash.

The differences in the appearance and behaviour of the basic sulphates of copper when they are precipitated by lime or soda are fully explained by these results (see p. 1990), for identical substances are not formed in the two cases, although the proportions of  $\text{CuO} \cdot \text{SO}_3$  are the same.

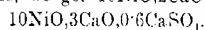
The behaviour of different alkalis towards other metallic sulphates indicates differences similar to those observed in the case of copper sulphate. This is evidently so with ferrous sulphate, the precipitate formed by lime being different in colour and much more bulky, when compared with that formed by soda, although with both alkalis the basicity is the same,  $10\text{MgO} \cdot \text{SO}_3$  (p. 1991). Ferrous sulphate, however, is not a convenient salt for investiga-

owing to its absorption of oxygen, and a few experiments were made with nickel sulphate instead.

TABLE V.—*Precipitation of Nickel Sulphate by Lime-Water.*

	Proportions taken.			Composition of precipitate.
	NiSO <sub>4</sub> .	CaO.	Na <sub>2</sub> SO <sub>4</sub> .	
1	10	8	—	10NiO, 28SO <sub>3</sub> , 0.11CaSO <sub>4</sub>
10	10	24	—	10NiO, 0.348SO <sub>3</sub> , 2.48CaO
40	10	48	—	10NiO, 0.498SO <sub>3</sub> , 3.61CaO
1	10	8	0	10NiO, 28SO <sub>3</sub> , 0.11CaSO <sub>4</sub>
10	10	8	17	10NiO, 1.748SO <sub>3</sub> , 0.164CaSO <sub>4</sub>
40	10	8	52	10NiO, 1.918SO <sub>3</sub> , 0.610CaSO <sub>4</sub>

The results are given in Table V. The most basic sulphate of nickel had been found to be 5NiO.SO<sub>3</sub> (see p. 1985), and this sulphate alone was examined. As seen from No. 40, it, like the corresponding copper compound (Nos. 2 and 3, Table I), contains no calcium sulphate, but in quantity so small that it might just be attributed to experimental error. On raising the amount of lime used beyond that required for the formation of the basic sulphate, we get, unlike the case of copper, an immediate and considerable reduction in the SO<sub>3</sub> present, the composition of the precipitate being substantially that of a double oxide of nickel and lime, a small amount only of calcium sulphate being present. Thus, in the two cases, we get 10NiO, 2CaO, 0.4CaSO<sub>4</sub> and



Whether the calcium sulphate would be entirely eliminated or not at a further increase in the amount of lime was not determined. When the basic sulphate is precipitated in the presence of excess sodium sulphate (Nos. 43 and 44), no sodium sulphate enters into its composition as it does in the analogous case with copper (Table III), but the proportion of calcium sulphate in it is increased instead, the partial saturation of the liquid by the sodium sulphate having, apparently, facilitated the abstraction of calcium sulphate from it. Clearly the tendency of basic nickel sulphate to combine with neutral sulphates is feeble as compared with that of the copper sulphate.

It will be seen that in Nos. 43 and 44 the analytical numbers indicate that some of the SO<sub>3</sub> has been abstracted from the basic sulphate. The mixtures were left standing for several days after a portion of the liquid had been withdrawn for analysis, and it was found that the remaining liquid gradually assumed a green colour, nickel passing slowly into solution again; doubtless some soluble double sulphate of nickel and sodium was being formed. The reaction of a certain amount of such a compound before the liquid

had been withdrawn for analysis would account for the detection of  $\text{SO}_2$  in the precipitate.

The examination of nickel sulphate having shown that it was unsuitable for an investigation which was in contemplation, the experiment was not pursued. The results, however, are sufficient to show that, whilst the basic sulphates of different metals exhibit certain points of similarity in their behaviour towards excess of alkali, each neutral sulphate, each metal shows peculiarities of its own, and the actual products could only be determined by a separate examination in each case.

#### *Summary.*

The substances formed on the addition of lime to copper sulphate in the preparation of Bordeaux mixture, are dependent on the proportion of lime used, and may be either (approximately) (1) or (2) the  $\text{CaSO}_4$  is concerned):

- (1)  $4\text{CuO}, \text{SO}_3, 0.06\text{CaSO}_4$ ,
- (2)  $5\text{CuO}, \text{SO}_3, 0.25\text{CaSO}_4$ ,
- (3)  $10\text{CuO}, \text{SO}_3, 1.3\text{CaSO}_4$ ,
- (4)  $10\text{CuO}, \text{SO}_3, 4\text{CaO}, \text{SO}_3$ ,

or possibly (5)  $10\text{CuO}, \text{SO}_3, 10\text{CaO}, \text{SO}_3$ , or (6)  $\text{CuO}, 3\text{CaO}$ ; that in most cases, probably being (4).

The fungicidal action of Bordeaux mixture seems to depend on the liberation of normal copper sulphate by the action of carbon dioxide on the basic sulphate. The action begins only after a certain lapse of time, the basic calcium sulphate having first decomposed before the basic copper sulphate is attacked. By the only sufficient lime to form  $4\text{CuO}, \text{SO}_3$ , the presence of basic calcium sulphate, and the consequent delay in the action, is avoided. In addition to this, the amount of normal copper sulphate liberated (for a given amount of copper sulphate taken), and the insoluble value of the mixture, will be two and a half times as great as if it consists of  $10\text{CuO}, \text{SO}_3, 4\text{CaO}, \text{SO}_3$ .

To obtain the basic sulphate  $4\text{CuO}, \text{SO}_3$ , one gram of crystalline copper sulphate in solution must be precipitated by adding 2.5 c.c. of lime-water. This mixture is rather more effective than the "normal" Bordeaux mixture, made with more than 40 times the amount of copper sulphate precipitated by milk of lime in excess.

When copper sulphate is precipitated by lime in presence of excess of sodium sulphate, the precipitate contains sodium sulphate as well as calcium sulphate; with the most basic sulphate the formula is  $10\text{CuO}, \text{SO}_3, 2(\text{Na}_2\text{Ca})\text{SO}_4$ , or  $10\text{CuO}, \text{SO}_3, \text{Na}_2\text{SO}_4, \text{CaSO}_4$ .

The basic sulphates of copper precipitated by soda contained

considerable amount of sodium sulphate, unless a large excess of lime sulphate is present in the liquid. They therefore differ essentially from those obtained with lime, although the basicity is the same in the two cases.

Nickel sulphate with lime gives a basic sulphate containing a little calcium sulphate, but if the lime is at all in excess, the nickel sulphate is deprived of most of its acid, the precipitate consisting essentially of a double oxide of nickel and calcium. If a large amount of sodium sulphate is present in the liquid, the precipitate contains more calcium sulphate, but the results are complicated by the nickel redissolving to form (probably) a double sulphate of nickel and sodium.

## CXCVI.—*Emulsions.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

The Sixth Report of the Woburn Experimental Fruit Farm (1900 and Spottiswoode, 1906) were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until the work here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, had arrived at an explanation of emulsification which is substantially the same as that given here.

### *Emulsions with Soluble Emulsifiers.*

When any liquid insoluble in water is mixed with the latter it breaks up into minute globules, as when it is forced through a fine sieve; these globules remain more or less permanently emulsified in the water if the water contains soap or some other emulsifying agent. The whole of the liquid, however, is not an emulsion, but is so called, but a mixture of the emulsion with excess of water; on standing, the true emulsion separates, and, if

the substance emulsified is lighter than water, rises to the surface. This is precisely analogous to the separation of cream from milk.

The time required for an emulsion to rise, and for the surface occupied by it to become constant, depends, naturally, on various circumstances, and varies between several days and many weeks. The line of demarcation between the emulsion and the external liquid is generally well marked, for the liquid becomes almost transparent, and, if it contains much soap, quite clear, whilst the emulsion is opaque. In many cases, the emulsion itself separates into layers, evidently of different composition, the line of demarcation between these being fairly distinct.

A rise of temperature facilitates emulsification with soap solutions, but there appears to be no difference between emulsions of the same composition when made at different temperatures. For each temperature and for each proportion of paraffin oil, there is a quantity of emulsifier which must be present ranges between certain definite limits; thus, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain from about 0.7 to 1.8 per cent. of potash soap; but for 40 volumes of oil to 60 of water, emulsification is possible with from 0.3 to over 25 per cent. of soap. The explanation of the existence of such limits (especially of the upper limit) will be discussed below, but it may be remarked that the above figures apply to only one particular soap, and that soap, even when of the same brand, vary greatly in their emulsifying power, it being difficult to obtain emulsification at all in some cases, even with the aid of heat.

Emulsification appears to occur suddenly: when soap is used, if the solution is not very strong, it is possible to judge immediately by the working of the syringe whether it has occurred or not; when it has not occurred, no continuance of the pumping, with altering other conditions, will produce emulsification.

The increase of viscosity on emulsification is easily explained by the great increase in the extent of the oil-water surface on the oil being reduced to minute globules. An ordinary emulsion, adding up to 70 to 80 per cent. of mobile paraffin oil, is as viscous as thick cream, and its viscosity increases with the proportion of oil present, even when that oil is a very light one, such as a lamp oil. With very high percentages of oil, the emulsion becomes practically solid, resembling a blanchemange. Emulsions containing as much as 99 per cent. of ordinary lighting oil have been made, the remainder being a 1 per cent. solution of soap. Such solid emulsions, however, cannot be obtained directly; they must be made by taking a weaker emulsion, and gradually increasing the proportion of oil, churning it after each addition. Even these strongest emulsions are true emulsions of the oil; that is, it is the oil which has

water, and the water, although so small in amount, which is the nucleus. There are no signs of the existence of an emulsion of water in oil. As a consequence of this, an emulsion (even a 1 per cent. one) will mix perfectly with water to form a weaker emulsion, but it will not mix with more paraffin, unless, of course, the paraffin is emulsified with it by further churning. Indeed, the addition of any paraffin in bulk to an emulsion eventually causes the de-emulsification of the whole, the globules of the emulsion being attracted by, and coalescing with, the mass of unemulsified paraffin. It is for this reason that an imperfectly made emulsion will eventually de-emulsify on standing, and so will a very strong emulsion, for it is generally an imperfect emulsion also, as it is doubtful that the whole of the paraffin in it cannot be churned up thoroughly. Spontaneous de-emulsification is usually a question of weeks or months, sometimes of years; possibly a very perfect emulsion would never de-emulsify spontaneously at all, but once de-emulsification has started, it progresses at an increasing rate.

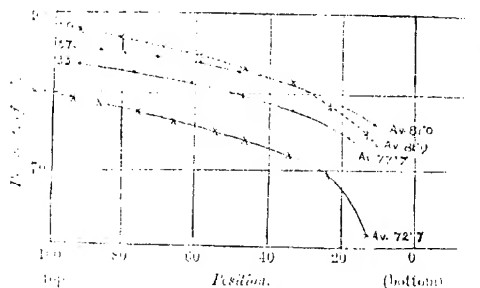
Strong emulsions, especially the semi-solid ones, are very bad conductors of heat. When one of them is heated in a wide test-tube it partially melts, de-emulsifies, and boils; but, although the boiling-point may be  $160^{\circ}$  to  $170^{\circ}$ , ebullition can be continued for several minutes, while a nucleus of the emulsion remains at a temperature far below  $100^{\circ}$  in the centre of the boiling paraffin. The water becomes gradually concentrated in this nucleus, and finally volatilises explosively.

Although one of these semi-solid emulsions, when kept in a closed vessel, will only gradually de-emulsify in the course of months, yet, when exposed to dry air, it will do so in a very short time; the edges of the lumps assume the appearance of a transparent, slightly blue jelly, and the whole liquefies in the course of a few hours. No such change occurs in moist air. It is evident, therefore, that the change to the transparent condition must be due to the loss of moisture, but it is difficult to see in what the change consists. The opaque emulsion appears to contain a few globules about  $0.0003$  mm. in diameter, but the bulk of it seems to be without structure, and, if composed of globules, as presumably it is, must be less than  $0.0001$  mm. in diameter. The transparent emulsion presents nothing at all visible under the microscope. Thus the difference between them seems to consist in the presence or absence of a few larger globules, but why these should disappear on drying the mass on exposure to air is not at all clear. The transparent jelly is as stable as the opaque emulsion, when kept in a closed vessel. On placing a portion of it in water it instantly becomes opaque, and gradually disseminates in the water, forming a very milky emulsion.

In a collection of close-packed spheres of uniform size, which that size may be, the volume of the spheres is 74.048 per cent. of the total volume of the mass; with an emulsion of uniform size, the volume of the oil would be less than this, as the spheres are not in actual contact, the separating film of medium being of appreciable thickness. But in emulsions, the spheres are not uniform in size, and therefore do not therefore appear to be any reason why the ratio of the volume of the oil to the total volume of emulsion should be of any particular magnitude. The ratios actually found, however, do not differ very widely from that for close-packed uniform spheres, being generally from 65 to 82 for every 100 volume of emulsion. This is independent of the proportions in which the oil and solution are taken to start with, so long as the former do not exceed 50 per cent.

In a number of experiments which were quoted in the W.

FIG. 1.



Oil, p. "Solar Distillate" in soap solution.

Report, the proportions for the oil to water composing the emulsions were found to be in the simple ratios of 2:1, 3:1, or 4:1. It was not possible to suggest any variation of this, and the results (although similar ones have been obtained subsequently) were probably fortuitous. It seems to be established by the fact that these emulsions were more or less in composition throughout their mass. The extent of this variation will be seen best by an inspection of Fig. 1. The emulsions were made by churning a 1 per cent. soap solution of "Solar Distillate," a paraffin oil distilling almost entirely between 210° and 350°, sufficient to make mixtures containing, respectively, 67.50 and 33 per cent. by volume of the oil. These were left undisturbed for twelve weeks, after which the emulsions, when disturbed to the top, contained, on the average, 81.0, 81.9 and 77.7 per cent. of oil in the three cases, respectively. The emulsions

drawn from top to bottom, removing for the purpose successive portions, and analysing each by adding to it a trace of acid, which emulsified it. The percentage (by volume) of oil diminishes gradually from the top of the column downwards, but very slowly at first, and more rapidly towards the bottom. The examination may well be extended to the very bottom of the column, as it is possible to remove the emulsion without drawing with it some of the heavy liquid from below. The three emulsions, as will be seen, do not differ much in composition, in spite of the different proportions of the oil and solution taken in their manufacture, and the differences as exist do not vary regularly with these proportions. In none of these cases were there visible any different zones, although they are often noticed, but the analysis gives some evidence of the existence of one in the case of the curve marked 67, for the first portions removed, embracing a quarter of the whole emulsion, gave the same values, namely, 81.7, 81.5 and 81.6 per cent. A more conspicuous instance of the arrangement in zones of equal strength has been mentioned below.

The emulsification of 50 per cent. of paraffin was repeated with 1 per cent., and with a 0.2 per cent. solution of soap as well. The results with the former, when plotted, were almost coincident with those with the 1 per cent. solution shown in the figure (marked 50); those with the 0.2 per cent. solution gave lower values throughout, and are represented by the lowest curve in the diagram. Differences, such as those exhibited between the emulsions prepared in Fig. 1, are, no doubt, merely due to differences in the number of the globules, and must be largely accidental. An examination under the microscope was sufficient to indicate that the average size of the globules in the emulsion giving the lowest curve was somewhat greater than that in the others, although no differentiation between these others amongst themselves was possible.

All emulsions contain globules of different sizes, and it is possible to form only a very rough estimate as to what is the average, or rather, most frequent, size of the globules present. With most of the oils emulsified in soap solutions containing from 5 to 0.5 per cent. of soap, the most frequent size seems to be about 0.5  $\mu$ mm. in diameter, but there are present some globules of almost four times this size, as well as smaller ones down to one-tenth of it, or less. In the semi-solid emulsions, as already stated, the globules are much smaller. Imperfect churning of the mixture gives rise to larger globules, but a dozen vigorous strokes of a syringe or a rose jet seems to be sufficient to break up the oil as far as is possible. A deficiency in the proportion of soap to the oil results in larger globules, and, if reduced too far, no perfect emulsification can be obtained.

APPENDIX.



The character of the oil, also, has an effect on the size of globules in emulsions with the lighter paraffins, such as the kerosene and motor spirits (sp. gr. 0.7 to 0.75), are more cream-like than those with lighting oils (sp. gr. 0.8) or "Solar" kerosene (sp. gr. 0.86); but with mineral naphtha and benzene, none of the above emulsions with these being exceptionally "creamed." With crude petroleum, sp. gr. 0.955 (which does not even shake), a very thick, unmanageable emulsion is obtained. Turpentine and olive oil do not emulsify with soap solution in any way as do the paraffin oils, a large portion of the mass remains unemulsified, and the line of demarcation between the two layers of different composition is not clearly marked. With turpentine that portion of the mixture which most resembles an emulsion contains only 5 to 6 per cent. of the oil, but with olive oil there is a small layer intermediate between the free oil on top and the solution at the bottom, which appears to be an emulsion, and it contains about 70 per cent. of oil.

Compared with the oil globules in cream, paraffin emulsions are more coarse-grained, and much less uniform. In cream, the globules are 0.005 to 0.006 mm. in diameter. They are, however, often taken together in groups, and are not distributed uniformly throughout the medium as in the case of paraffin emulsions.

So long as thorough emulsification has been produced, there does not appear to be marked variations in the size of the globules, an emulsion throughout the mass; the only difference observed between the upper and lower layers is, that in the former the globules are more closely packed than in the latter.

Other soluble substances, besides soap, will act as emulsifiers; paraffin and some of them are used practically in America. Starch, milk and corned flour are amongst the latter, and the author has also confirmed the results obtained with solutions of glue, starch, albumen, casein and extract of quillaia bark. All these substances give emulsions more or less closely resembling those of soap, but they all appear to be inferior to the latter as regards the fineness of texture of the product, and, consequently, the emulsion separates from the excess of liquid more rapidly. With soap and quillaia, this is notably so, and with proportions of these materials which have been recommended for use (0.025 per cent. of quillaia) emulsification is so unsatisfactory that de-emulsification after twenty-four hours, whilst, if the proportion of paraffin in the mixture is large (67 per cent.), only partial emulsification is obtainable. With some of the other substances mentioned, for example, milk, it is not possible to obtain a strong emulsion unless the paraffin is added gradually, churning after each addition.

*De-emulsification.*

The de-emulsification of an emulsion may be brought about, (1) by the presence of unemulsified paraffin, as already mentioned; (2) by adding a liquid, such as alcohol, in which the paraffin and water are both soluble; or (3) by destroying the emulsifier. The most convenient de-emulsifier to use when determining the percentage of oil in an emulsion made with soap is a small quantity of mineral acid. With a very strong semi-solid emulsion, a mere drop of hydrochloric acid is sufficient to convert it almost instantly into a mass of liquid oil, with a few drops of water below it. Any strong salt produces de-emulsification, owing to the conversion of potassium soap into the comparatively insoluble sodium soap. The de-emulsifying action does not appear to be in any way dependent on the de-emulsifying agent being an electrolyte, for potassium salts have no effect on emulsions in potassium soap, and even hydrochloric acid will not produce de-emulsification (as will be shown experimentally) in cases where the emulsifying agent is not destroyed.

In the Woburn Report, it was shown that a paraffin emulsion containing 2 per cent. of caustic soda possessed valuable insecticidal and detergent properties, but the practical de-emulsification produced by the soda detracted from the merits of the mixture, making much agitation of it necessary during use, and rendering a fine distribution difficult. The amount of paraffin recommended for this wash was six volumes per cent., and the soap was reduced to 0.5 per cent., so as to minimise the bulk of solid thrown down when the soda was added. From such a mixture, the soda soap readily separates as a flocculent mass, which rises to the surface, and with the paraffin, and forms with it a bulky scum which occupies about one-third of the total volume. This scum, as will be seen below, is what may be termed a quasi-emulsion. It varies considerably in its nature according to the character of the soap used. With one example of soap in our possession (although of the same kind as other samples) it is scarcely distinguishable from a paraffin emulsion. (Caustic potash, it may be mentioned, cannot well be used as a substitute for caustic soda, on account of its price, and, when soap is present, the soap is gelatinised, forming a magna opus which cannot be used for spraying.)

On account of the disadvantages attaching to the separation of soap from caustic emulsions, some more suitable emulsifier was sought. Gum arabic or glue was used, the addition of caustic soda produced no de-emulsification, and the same occurred to a slight extent

with egg albumen or starch; milk, also, is not very satisfactory, even when caustic soda is not present. Attention was turned to the possibility of obtaining an insoluble substance to act as emulsifier. This did not seem impracticable, the fact that lime had recently been stated to produce emul-

### *Emulsions with Insoluble Emulsifiers.*

Lime united with petroleum was first used for spraying purposes under the name of "limoid." A certain magnesian lime of a certain character was found to absorb double its weight of petroleum, and the mixture thus obtained, disseminated in ten to nine times its volume of water, was used as a spray-fluid. Subsequently it was found that any ordinary lime would not emulsify with petroleum, and the proportions recommended in America are 2.2 gram of quicklime to 11 c.c. of kerosene and 100 c.c. of water. There does not appear, however, to be any reason for adhering to these particular proportions, for they may be largely without materially affecting the results.

Much work was done on these lime emulsions before a clear idea was obtained as to their real nature, but only a brief reference to this work will be necessary here. Limes from various sources were examined, and all gave substantially the same results as the oxide prepared from marble, to which the following remarks apply.

On churning up lime with paraffin and water, a sort of emulsion is obtained, which either rises or sinks in the excess of water according to the proportions used. The separation of the oil from the excess of water is much more rapid than in the case of an emulsion in soap solutions. By suitably adjusting the proportions an emulsion of a specific gravity of unity can be obtained, in which there is no sinking or rising, so long as the proportion of water is not more than 50 to 70 per cent., but, on dilution, part of the emulsion rises and part sinks; both these parts contain oil, but the upper part most.

The volume occupied by emulsions with lime, and the percentage of oil contained in them, present no features analogous to those in soap solutions, for here the lime itself occupies a large part of the total volume, and by its weight it drags down the oil, thus preventing any close packing of the oil globules.

The general behaviour of these lime emulsions suggests that they are merely gross mechanical mixtures of lime and paraffin, and not true emulsions. An examination under the microscope

Moreover, the oil globules present in them are very large, and show great variations in size, being, under the most favourable conditions, ten times the diameter of the globules in a soap emulsion. They appear to be merely caught by, and entangled in, the particles of lime. Moreover, their size, instead of being practically constant, independent of the proportions of emulsifier and of oil, as in the case of soap emulsions, seems to be entirely dependent on the amount of lime. If the lime is not present in considerable quantity, the globules are so large that they become visible to the naked eye, the mixture then being an evidently non-homogeneous mixture, which has no title to be called an emulsion. With a further reduction of the amount of lime, or an increase in that of oil, a separate phase of the latter appears.

In one series with "Water White" oil in proportions ranging from 25 to 67 per cent. by volume, and with lime equal to 2.2 to 6.6 Gm. per 100 c.c. of the mixture, the product became visibly homogeneous when about 35 per cent. of paraffin was reached. A lower limit (about 30 per cent.) was obtained in a similar series with "Solar Distillate." In another series with the latter oil the paraffin was kept constant at 50 per cent., and the amount of lime varied, an apparently homogeneous emulsion was obtained until the lime reached 10 grams per 100 c.c. of the mixture. With a very light oil, such as motor spirit, no homogeneous emulsions could be obtained at all, even when the percentage of lime exceeded that of the oil.

Other finely-divided substances have been examined, and found to give results similar to those with lime, although minor peculiarities are noticeable in the case of each substance: plaster of Paris, precipitated chalk, precipitated silica and alumina were amongst those which more closely resembled lime in their behaviour.

"Mineral mixtures of such substances with paraffin may consequently be termed quasi-emulsions, for, with certain proportions of the solid and the paraffin, they approximate to emulsions in character, and may serve the same practical purposes as true emulsions. Yet, as will be shown immediately, they are essentially different in constitution from true emulsions.

A quasi-emulsion with lime may be mixed with caustic soda without any change being produced, beyond rendering it somewhat more fluid, and it can be mixed with other insecticides and fungicides, notably with copper sulphate, thus giving it an advantage over emulsions with soap. On the other hand, it presents decided disadvantages, in the coarseness of the emulsion produced, the large proportion of lime required, and the difficulty of spraying, with the consequent clogging or destroying the nozzles of the machines.

When copper sulphate was added to the lime before emulsification, it was noticed that the emulsion produced was altogether different from that with lime alone, and, following up this observation, it was ascertained that the basic sulphate of copper, produced by the action of the lime on the copper sulphate, is, by itself, capable of emulsifying paraffin and water, almost as finely and much more easily than soap. If excess of lime is to be avoided, and all the copper is to be precipitated, the basic sulphate may be obtained by adding about 134 c.c. of lime-water to every 100 c.c. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; if otherwise, solid lime may be added to the sulphate solution, and, although the quantity of pure lime precipitated is only one-eventh of the weight of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , it is advisable in practice to increase this to one-third if commercial lime is used, to make this into a milk, running it through sacking into the sulphate, so as to eliminate any gross particles. On adding paraffin oil to this, and churning, one stroke of the syringe is sufficient to produce a perfect emulsion, and even shaking the mixture will form an emulsion good enough for practical purposes.

Such an emulsion possesses nearly all the characteristics of one made with soap, except that, there being a heavy and bulky precipitate present, the volume occupied by the emulsion proper does not depend solely on the oil globules, and the emulsion may sink or sink in the excess of solution according to the proportions of precipitate and basic sulphate used. It generally forms a very thick cream, with a perfectly clear-cut line of division between the cream and the excess of liquid. In texture, it appears under the microscope to be identical with emulsions in soap, although the average size of the component globules is about twice as great. Nothing of the mass of oil globules can be seen, as the particles of basic sulphate are generally too small to be visible. If enough of the basic sulphate is present, the proportion of paraffin can be increased to a very high point, the emulsions becoming thicker, until they are almost solid. With an insufficient proportion of basic sulphate, emulsification is imperfect; the minimum with strong emulsification "Solar Distillate" is, approximately, 1 gram of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  converted into basic sulphate, for every 120 c.c. of oil; if the emulsion is weak, the proportion of basic sulphate required is less. In the case of the sulphate of iron, which, as will be mentioned immediately, may be used in the same way, the proportions are of the same order of magnitude, 1 gram of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  being required to emulsify about 200 c.c. of oil to make a 6 per cent. emulsion, 100 c.c. to make a 20 per cent. emulsion, and 30 c.c. to make a 60 per cent. emulsion.

To obtain satisfactory emulsions with the basic sulphate

is necessary to use a paraffin oil of high boiling point, such as a "Solar Distillate"; with ordinary lighting oil, emulsification is not possible, unless the proportion of basic sulphate is very large, and even in ether spirit the paraffin is never more than partially emulsified.

For practical purposes, an emulsion with basic copper sulphate has many advantages over one made with soap. In the first place, it is a fungicide as well as an insecticide, for it contains all the elements of Bordeaux mixture; secondly, it is very bulky, and its tendency to separate from the liquid is much less. If the copper sulphate taken is 1.6 grams to 100 c.c. (the quantity used in a normal "Bordeaux mixture made with milk of lime"), 3.5 c.c. of "Solar Distillate" (sp. gr. 0.858) makes with it an emulsion which neither sinks nor rises, and if the "Solar Distillate" is reduced to 6 c.c., as it might be for winter use, or reduced to 1 c.c., for summer use, the tendency to rise or to sink, respectively, will be but small, the slightest agitation being sufficient to keep the emulsions disseminated throughout the liquid. With Bordeaux mixture made with lime-water, as recommended in the preceding communication (p. 1937), only 0.7 gram of copper sulphate to every 100 c.c. is used, and 1.4 c.c. of "Solar Distillate" will convert this into an emulsion which will neither sink nor rise, and which is of a most convenient strength for general summer use.

Besides the facility and certainty with which these emulsions can be made, they possess the advantage of being much more permanent than emulsions made with soap. No single instance has yet occurred in which any one of them has de-emulsified spontaneously. They can be mixed with caustic soda (2 per cent. being usually used) to make a detergent winter wash, without becoming emulsified, as in the case of soap emulsions.

In connexion with the use of soda with these emulsions, one or two points must be mentioned. Copper hydroxide will not emulsify so well as the basic sulphate does, and, although caustic soda precipitates the basic sulphate  $4\text{CuO},\text{SO}_3$ , when added in the proper proportions, excess of alkali converts it into the hydroxide, so that it cannot be used for the preparation of a caustic copper emulsion. But if the  $4\text{CuO},\text{SO}_3$  is precipitated by lime, and then dissolved, the excess of soda may be added without producing any perceptible change; it is only after the lapse of a month or more that an emulsion made in this way will show any signs of the presence of copper hydroxide, and begin to blacken. This difference in behaviour, according to which alkali is used for the precipitation, has naturally caused much perplexity, until the investigation of the basic sulphates, detailed in a previous communication, had

shown that the precipitate with lime is not merely  $4\text{CuO}\cdot\text{SO}_4$ , but a compound of that sulphate with calcium sulphate.

If fungicidal properties are not required in the caustic, ferrous sulphate may be substituted for the more expensive copper sulphate. The emulsions with the iron salt have certain advantages over those with the copper salt. The oil globules in the smaller (about one-third to one-fifth of the diameter) and the emulsions are more bulky, and separate from the excess of oil more slowly. Moreover, ferrous hydroxide, unlike copper hydroxide, is itself capable of emulsifying, and hence the precipitation with lime may be dispensed with and the caustic alone be used. A much finer emulsion, however, is obtained if lime is used as the precipitant, as in the case of copper. When lime is used, that required for the precipitation, as well as the 2 per cent., may all be added to the iron sulphate at once by emulsifying with paraffin. The basic ferrous sulphate, or ferrous hydroxide, as the case may be, is, of course, partially oxidized, and the emulsion becomes nearly black. On keeping it in a closed vessel, it sometimes (especially if excess of lime is present) becomes almost colourless, organic substances in the paraffin apparently reducing the ferric compounds; on exposure to air, it becomes orange-red, ferrous ferrie oxide being formed. These changes do not appear to affect the emulsification.

One drawback to the copper emulsion is that it cannot be prepared in a concentrated form like a soap emulsion. The proportion of oil present may be increased, but not that of the copper; lime must be used as the precipitant, and, if this is added to a strong solution of copper sulphate, the precipitated basic sulphate forms a compact mass which will not emulsify the oil present. With ferrous sulphate, however, where soda can be used as precipitant, this difficulty does not exist, and it is possible to prepare an emulsion of which 100 c.c. contain 60 c.c. of oil, this being 12 times the strength generally required for spraying. The quantity of iron which can be got into such a strong emulsion, however, is not large, and, consequently, the emulsion is light, and rises to the surface when diluted, necessitating agitation during use.

Some of the copper emulsions were examined by analysis in the same way as soap emulsions. It will be sufficient to quote the results with one of them only, and these are given in the accompanying table and in Fig. 2. The mixture taken for emulsification contained 20 c.c. of "Solar Distillate" and 0.18 gram of copper in the form of sulphate, per 100 c.c. Portions of the emulsion were analysed throughout their mass after twenty-four hours, five days, and twelve weeks, the average proportions of oil in the

33.3, 38.0 and 42.6 per cent., respectively. The emulsion becomes more concentrated as time elapses, and, at the same time, the curve representing its composition becomes flatter, though in all cases there is a rapid fall in concentration towards the bottom of the column. The most marked feature, however, is the alternate arrangement of the emulsion into layers of uniform composition, which, although not visible as separate layers to the eye, are made evident by the analysis. Such an arrangement has

FIG. 2.

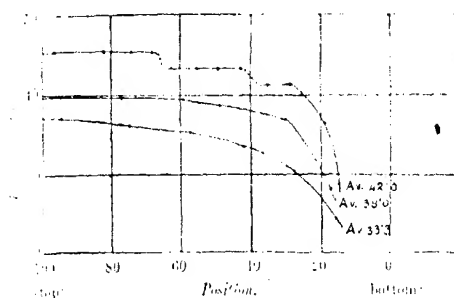


Fig. 2. Composition of emulsions. "Solar Distillate" with basic copper sulphate.

already been noticed in the case of emulsions with soap. As will be seen from the table, the percentage of basic sulphate in the emulsion decreases from the top to the bottom with the percentage of oil, but not so rapidly as the latter, so that the proportion of it

TABLE I.  
Composition of Emulsions of "Solar Distillate" with Basic Copper Sulphate.

Time, days.	After 10 days.		After 12 weeks.		Oil.	CuO.	CuO : Oil.
	Oil.	Position.	Oil.	Position.			
10	97.8	100-85	40.1	100-93	15.3	0.498	0.967 : 100
	97.0	85-69	39.9	93-86	43.5		
	95.4	69-53	39.4	86-79	45.3		
	93.5	53-37	38.7	79-72	45.3		
	90.1	37-22	36.7	72-66	45.3		
20	82.5	22-8	26.1	66-60	43.4	0.594	0.916 : 100
				60-53	43.3		
				53-47	43.1		
				47-39	43.3		
				39-31	41.3		
				31-25	41.3		
				25-22	40.6		
30				22-17	37.2	0.352	1.671 : 100
				17-11	28.5		



to the oil increases downwards. It is noticeable, however, that the increase is very small; in spite of the differences in specific gravity, about 2.5 and 6.86, there is very little separation of the two substances, and the union between them must, therefore, be of a decidedly intimate character.

### *The Nature of Emulsions.*

It is evident that emulsions with basic copper sulphate are strictly similar in nature to those with soap, and are quite distinct from the quasi-emulsions with lime. Many other substances act in a manner similar to basic copper sulphate, but few of them act so effectively. The action, however, is not distinctive of basic substances; one of them, such as the basic sulphates of copper, iron and zinc, form true emulsions, whereas those of zinc, aluminium and calcium form quasi-emulsions only; other substances when freshly precipitated behave in a similarly arbitrary manner, calcium arsenate, for instance, forms a good emulsion, whereas with barium sulphate signs of emulsification are obtained. On the other hand, no connexion between emulsification and the nature of the metal can be traced; copper hydroxide will not emulsify, although basic sulphate will, whereas both ferrous hydroxide and basic ferrous sulphate are good emulsifiers. Nor is the minuteness of the precipitate any guide to its emulsifying power; precipitated aluminium silicate, although very bulky, does not emulsify, nor does gelatinous silica. The colloidal condition of the substance, also, has no influence on the results, for paraffin will emulsify in a dialysed solution of silica.

The view which the writer was eventually led to adopt of emulsification, was that it depended solely on the size of the globules constituting the precipitate. When the oil is broken up into small globules by being forced through the syringe, and the globules find themselves in the presence of a number of very much more minute solid particles, the latter will be attracted by the globules, and will form a coating or pellicle over the surface, preventing them from coming in contact and coalescing with their neighbours. Whether gravitation alone is sufficient to accomplish such a result, or whether other forces come into play, must be left for others to determine, but that the solid particles do collect closely round the globules, there can be no doubt, for they are often be seen under a powerful microscope. With basic copper sulphate this is so, although the particles are so nearly ultra-microscopic that they cannot be resolved sufficiently to admit of an estimate being made as to their actual size; with basic iron sulphate

are still smaller, and quite invisible, but their aggregation into the globules is evident from the brown ring encircling the surface.

Further evidence that the globules must be enveloped in some substance is found in the fact that these emulsions do not make the containing vessel oily; indeed, this forms a very good distinctive test between a true emulsion and a quasi-, or imperfect, emulsion. The same test may be varied by dropping a little of the liquid into a glass of water; if unemulsified paraffin is present, the surface of the liquid becomes oily, but not so if the paraffin is present as a true emulsion.

An emulsion on this view, however much it is diluted with water, undergoes no de-emulsification, whereas with a quasi-emulsion, where the oil simply have oil globules entangled with the gross particles of a solid, it should always be possible to separate the greater part of the oil by adding enough water. This, as a matter of fact, is found to be the case. It is also possible to remove the oil from a substance with which it forms only a quasi-emulsion, by adding another substance with which it forms a true emulsion. Thus a quasi-emulsion of lime and paraffin of a suitable strength will rise in a glass to the surface of water, but, if some sodium arsenate is added, lime arsenate is formed, and, as this is a true emulsifier, it forms an emulsion with the oil, and rises to the surface, whilst the lime, freed of the oil, sinks to the bottom.

Neither in the case of a true emulsion nor in that of a quasi-emulsion does the nature of the menstruum appear to have any influence on the emulsification, so long as it does not react chemically with the emulsifier or the oil; a variety of salts may be added in water containing an emulsifier without affecting the emulsion, beyond making it in some cases (notably when caustic soda has been added) more viscid, due, no doubt, to an increase in the coefficient of friction. Even strong mineral acids have no effect in a case such as that of clay (some clays will act as emulsifiers), where the solid emulsifier is insoluble in acids.

Although emulsions and quasi-emulsions are radically different in their nature, various substances will yield results showing every possible gradation between the two, for the simple reason that substances may consist of particles of every gradation of magnitude, small enough to emulsify the oil globules, and others too large to do so, and therefore form quasi-emulsions. In the same way, there is every gradation between a quasi-emulsion and the complete separation of the oil and water into independent layers.

The power of emulsifying, not being an inherent property of the substance, but simply depending on the size of its particles, it

follows that this power should be destroyed by aggregation; this is so, can easily be proved. The basic sulphates, *etc.*, arsenate, Oxford clay, &c., all of which form true emulsions, are found to be quite incapable of doing so after they have been finely powdered; however finely they may then be powdered.

The average size of the globules in an emulsion seems to be dependent on the size of the particles of the emulsifier. The particles of basic ferrous sulphate are more minute than those of basic copper sulphate, and the emulsion is decidedly finer; as with nickel basic sulphate, both the particles and the globules are of about the same size as with the copper salt, and with cadmium and zinc basic sulphates the particles are greater, the emulsion is very coarse, being to a large extent only a suspension. Whether, however, the chemical nature of the emulsifier is altogether without effect on the results or not, and whether the size of the particles is the sole determining factor, it is impossible to decide with certainty, without a more extended series of experiments, aided by better eyesight and better microscopic appliances than were available in the present case. It seems, however, that the attraction between the oil globules and the solid particles is sufficient to modify somewhat the chemical behaviour of the latter. The basic sulphate of copper precipitated by lime, and treated with excess of caustic soda, will blacken after a few days, owing to the formation of copper oxide, but, when emulsified in "Solar Disinfectant" this blackening does not commence nearly so soon; it is more rapid when a lighting oil is used, this forming a coarse emulsion, and much more so if petrol is used, when the emulsion is very imperfect indeed. Similar evidence is obtained in making emulsions with the same oil, but using different proportions of it; that which contains more oil will blacken more slowly. Analogous results are obtained with ferrous sulphate, the colour of the emulsion, due to different degrees of oxidation, differing according to the nature of the oil used. It is possible, however, that in these cases the retardation of the action of the soda on the basic sulphate, or the oxidation of the compounds present, may be due to a chemical action of impurities in the oil.

A few instances exist which seem at first sight to negate the view that the power of emulsifying is conditioned by the nature of the solid particles. Thus, precipitated sulphur, purple of Cassius, and ferric ferrocyanide, all of which are in an extreme state of subdivision, will not emulsify paraffin at all. The behaviour of sulphur gives a clue to this result. When flowers of sulphur are thoroughly incorporated with water, are churned with paraffin, the latter abstracts the whole of the sulphur from the water, and

and a greasy mixture, which sticks obstinately to the syringe, the warming vessel, &c., the paraffin evidently wetting the sulphur in a way which the water does not. A similar effect is observed in the case of purple of Cassius and ferric ferrocyanide; although paraffin is not emulsified at all, it abstracts the whole of these dyes from the water, becoming intensely coloured by them, leaving the water colourless, just as if they dissolved in the paraffin. The view therefore that emulsification depends solely on the minuteness of the solid particles must be so far modified as to apply only to such solids as are wetted more easily by water than by oil, otherwise there is no emulsification at all.

The explanation of emulsification here advanced would hardly be acceptable unless it could be applied equally to cases where the emulsifier is a liquid, and there seems to be but little difficulty in doing so; for these liquid emulsifiers are all substances which, under the conditions obtaining, partly separate from the solution, and yield sufficient solid particles to form a pellicle over the oil droplets. Liquid emulsifiers are all distinguished, so far as we are concerned, by a feeble affinity for water; in many cases they are, or contain, protein substances, which, as Ramsden has shown, form a skin of solid matter at any boundary between the solution and the fluid, whether liquid or gaseous. In other cases, the deposition of some particles of the solid would result from this solid being insoluble in the paraffin. The water in the neighbourhood of a paraffin globule would become impregnated with paraffin, and the dissolved substance, having but a small affinity for water, would be thrown out of solution. Solutions of eggalbumen, glue and starch, when covered with a layer of paraffin, all form a slight opaque pellicle at the junction of the two liquids. In this way, each globule of oil could obtain for itself the solid particles necessary for its emulsification, but these particles would, no doubt, often be redissolved, and others, in their turn, would be deposited, and, in the course of these changes, opportunities would occur for the coalescence of neighbouring globules. This explains why emulsions in soap will generally emulsify spontaneously, if left long enough, whereas emulsions with a really insoluble emulsifier seem to be quite permanent.

Formed in this way by solid deposited *in situ*, an emulsion in soap, containing such substances, would naturally be more fine-grained, and the solid particles would be more closely packed, than in cases where a finely formed precipitate is the emulsifier. A rise of temperature would mean an increase in the volatility of the oil used, would result in the deposition becoming more permeated with paraffin particles, and depositing more of the dissolved soap, thus facilitating emulsification. With soap, a rise of temperature does facilitate emulsifica-

tion, and an increase in the volatility of the oil sometimes does the same (pp. 2002, 2006). With insoluble emulsifiers, however, neither a rise of temperature nor an increase in volatility favours emulsification; indeed, the latter materially hinders it (p. 2002). It is, no doubt, to the more volatile oils being more mobile.

Whether any soluble inorganic substance exists which can emulsify oil in the same way as does soap, appears to be doubtful; it is certainly probable that any substance which is crystalline would be incapable of emulsifying. Saturated solutions of calcium hydroxide and sulphate, as well as of sucrose, dextrin, and dextrin, have been tried, with negative results.

With soap, the particles requisite for emulsification are also provided in another way: for when soft soap is dissolved in water, or when a strong solution of it is diluted, a considerable amount of a very fine deposit is obtained, and this is often in a minute state of division that it remains suspended in the liquid for weeks. The separation of this precipitate on dilution, and its redissolution on concentration, explains a fact previously noted (p. 2012), which otherwise would present considerable difficulties, namely, that for each proportion of paraffin and water the amount of soap necessary for emulsification must not only be in excess of a certain minimum, but also must not be in excess of a certain maximum. The existence of the superior limit is explained if emulsification depends to any large extent on the presence of the particles precipitated by dilution, for the tendency to deposit these particles would be less in stronger than in weaker soap solutions.

(It should be mentioned, however, that a superior limit does not seem to exist in the case of all soaps. This is not surprising, as soaps vary largely in composition, even when they are of the same brand, and from the same factory, and they differ considerably in their behaviour on dilution.)

That the formation of a pellicle of solid particles over the oil globules affords an explanation of emulsification, is, as has been mentioned, the conclusion to which Dr. Ramsden also was led, and the view that such a pellicle exists in the case of the oil emulsion in milk was advocated long ago. So far as can be seen, this view seems to harmonise with all the observed facts.

#### *Behaviour of Various Substances.*

It would be tedious and unprofitable to describe at length the behaviour of the many substances which have been examined, as regards their emulsifying powers; but they may be briefly enumerated, classing them roughly into those which give the

those which give imperfect emulsions or quasi-emulsions, and those which do not seem to emulsify at all. In some cases, however, it is rather difficult to decide in which class to place a particular substance, and, in others, the method of preparation affects the behaviour of the substance in question.

*Emulsifiers.*—Amongst soluble, or partially soluble, substances soft soap seems to be the best; dissolved starch, milk and gum are good, although the latter forms a flocculent, and not a true emulsion, and milk gives rise to solid clots; glue emulsifies oil, and so does egg albumen, but the emulsion with the latter is very frothy, owing to enclosed air bubbles; saponin and quillaia give good emulsions when the proportion of oil present is not too small.

Amongst insoluble emulsifiers, the basic sulphate of iron is the best, followed by those of copper and nickel; the basic sulphates of barium and aluminium generally give good emulsions at first, but precipitation of the particle seems to occur, and causes partial de-emulsification. Ferrous hydroxide and the higher oxides of iron precipitated are good. The precipitate obtained by adding sodium arsenate to copper sulphate is a very good emulsifier, so are calcium arsenate and calcium arsenate when first precipitated, but the latter soon become crystalline, and de-emulsification follows; calcium arsenate, freshly precipitated, is good, and zinc oxychloride, and zinc chloride, is fair, although the emulsion with it is flocculent; some clays (unheated), such as Oxford clay, give good emulsions, but they, naturally, contain many gross particles which sink to the bottom unemulsified; ferrous hydrosulphide gives a good emulsion if the proportion of oil present is small.

*Substances producing Quasi-Emulsions, or producing Partial Emulsions.*—Lime, silica, alumina, plaster of Paris and many fine earths which have been dried; also the following precipitated earths when in the liquids from which they have been precipitated: basic cadmium sulphate, magnesium hydroxide, copper hydroxide, the basic sulphates of zinc and aluminium, stannous chloride, purple of Cassius, lead arsenate paste (a commercial preparation for insecticidal purposes), some clays and brick earths, ferrous sulphide, ferrous hydrosulphide (unless the proportion of oil is very low), and precipitated soda soap.

*Substances showing little or no Power of Emulsifying.*—Precipitated barium chloride, lead sulphate, barium sulphate, neutral silica, sulphur precipitated by adding acid to sodium thio-sulphate, flowers of sulphur and dried Paris-green (in both of these the powders seem to absorb the oil, forming a sticky mass which adheres to the syringe and containing vessel in an obsti-

nate manner); an alcoholic solution of resin precipitated by water (in the same manner); ferric ferrocyanide, ferric ferrocyanide, and purple of Cassius (in the last two cases the precipitate is carried up by the oil in small quantities to colour it strongly); and, lastly, any coarse precipitates, fine powders, especially when present in small proportions.

### *Summary.*

When paraffin oil is churned up with a solution of soap, an emulsion is formed which rises to the surface and contains 65 to 82 per cent. by volume of oil. Emulsions containing as much as 99 per cent. can, however, be obtained, and these are so stiff as to be almost solid. The character of the oil does not much affect the results, neither does the extent of the change in the proportion of soap, so long as this proportion is within the limits.

The amount of oil in an emulsion which has arrived at a state of equilibrium decreases somewhat from the top downwards, and there is often a tendency to arrange itself in layers of approximately uniform composition.

Solutions of other organic substances, such as glue, flour, starch, albumen, saponin, &c., act as emulsifiers for paraffin. All these emulsions will often spontaneously become de-emulsified, and this occurs at once if the emulsifier is destroyed; for example, if an acid or any sodium salt is added to an emulsion with electrolytes, as such, seem to have no de-emulsifying action. The addition of unemulsified paraffin to an emulsion will gradually de-emulsify the whole.

The oil globules in an emulsion are probably prevented from coalescing by being enveloped in a pellicle consisting of particles of solid much more minute than the globules themselves. These solid particles would be derived from the solution, which in every case contains a substance with but little affinity for water. Insoluble in paraffin, it being, therefore, precipitated in the neighbourhood of the paraffin globules.

Apparently, a precipitate consisting of any insoluble solid which is wetted more easily by water than by oil, if in a sufficiently fine state of division, will equally act as an emulsifier, and in these cases it is possible under a microscope to see the coating of solid particles which envelop the oil globules. Emulsions made with an insoluble emulsifier are in every respect similar to those made with soap, &c., except that they never seem to de-emulsify spontaneously; spontaneous de-emulsification being, no doubt, due to the fact that the solid particles, as in the case of soap, migrate

and are continually being redissolved and reprecipitated, affording opportunities for the coalescence of the oil globules. The basic sulphates of iron and copper are amongst those substances which give excellent emulsions. They may be formed by adding lime, or lime-water, to the normal sulphates, and then the emulsion, when the slightest churning, or even shaking of the mixture, produces emulsification. Besides the case of manufacture, there is the absence of spontaneous de-emulsification, these emulsions possess the advantage of not being decomposed by the addition of caustic soda, as are emulsions with soap, and caustic soda is required when the emulsion is used as a winter wash for trees. When the copper salt is used, the emulsion possesses all the fungicidal properties of Bordeaux mixture.

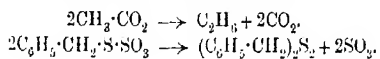
Many other precipitated substances act as emulsifiers, but this property is destroyed as soon as they have been dried, or have by other means been deprived of their fine grained structure.

Solids which are not sufficiently fine grained to emulsify will, in many cases, when present in considerable proportions, form quasi-emulsions. In these, the particles of oil are merely entangled with particles of solid, and may be separated from them by such means as dilution with water. Lime is an instance of a substance which forms a quasi-emulsion which can be used for spraying purposes. Other substances, including many recently-formed precipitates, and, probably, all crystalline solids, seem to be capable of forming even quasi-emulsions.

## XVII.—*The Electrolytic Preparation of Disulphides.* *Part I. Dibenzyl Disulphide and Diethyl Disulphide.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

In a preliminary note (Proc., 1906, 22, 260), we have shown that the electrolysis of a solution of sodium benzyl thiosulphate yields *dibenzyl disulphide*. The electrolysis was carried out in a beaker, the cathode consisting of a sheet of platinum foil lying close to the sides of the vessel, the anode being a piece of stout platinum wire. This apparatus was used because it was thought that the electrolysis would take place in a similar manner to that of sodium acetate, a constant current density at the anode being necessary:



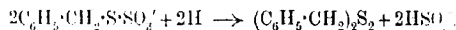
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When a pure aqueous solution of sodium benzyl thiosulphate was used, the solid dibenzyl disulphide obtained was contaminated with a quantity of a pungent oil, which, from its behaviour towards sodium, was benzyl mercaptan. The formation of the latter was probably due to the decomposition of some of the complex thiosulphate residues formed during the electrolysis. The addition of sodium bicarbonate or carbonate, in quantity sufficient to neutralise any acid formed, completely prevented the formation of any mercaptan, and the product was then a white solid, which investigation proved to be dibenzyl disulphide. Consequently, in all later electrolyses, an equivalent weight of sodium carbonate was added to the complex sulphate taken.

All the earlier experiments were carried out in the apparatus described, that is, in an undivided cell, and the results were satisfactory yields amounting to even 80 per cent. of the theory (calculated on the thiosulphate compound taken) being obtained, that it was assumed that the action was exactly as had been anticipated. However, replacing the thiosulphate compound in the anode chamber of a divided cell, it was found that no disulphide was formed, whereas on carrying out the electrolysis with the thiosulphate compound in the cathode compartment, the usual yield of the disulphide was obtained. The formation of the disulphide is thus due to reduction at the cathode, higher sulphite ions being produced at the same time according to the equation:



One would be inclined to suppose that the product of reduction at the cathode would be the mercaptan, since it is usually stated that disulphides are very readily reduced, but in none of the experiments with platinum electrodes and an equivalent quantity of sodium carbonate were used has any mercaptan, as indicated by the odour, been formed. This has also been the case in a few experiments with a lead cathode, at which electrochemical reductions generally take place much more readily than with platinum electrodes, has been found. Fielder and Bernoulli (*Zeitsch. Elektrochem.*, 1907, 13, 416) found that the reduction of *p*-toluenesulphonyl chloride to *p*-toluenemercaptan takes place quantitatively when lead cathodes and a low current density are used; electrodes of nickel or platinum did not give such good results.

In the present case, it seems as if the  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{S}\cdot$  residue which is formed when the link between the two sulphur atoms in the benzyl thiosulphate is broken, combines with another such residue before reduction to the mercaptan can take place. That the two residues will unite in this manner was shown by Bunge (*loc. cit.*)

3, 265, 911), who prepared disulphides (ethyl, amyl, and phenyl) by the electrolysis of alcoholic solutions of the sodium mercaptans. The disulphides were formed at the anode.

Further experiments to find out the conditions necessary to obtain the best results showed that, when the pure sodium benzyl thiosulphate is used, there is no great advantage in having the anode and cathode in separate compartments, so that the apparatus required is very simple. Also, the yield of disulphide is improved by using a concentrated solution, a low current density at the cathode, and a temperature of 60–70°. As will be seen from the figures given in the experimental part, the lower the current density at the cathode the better is the yield of disulphide, but, since with very low current densities the time necessary for electrolysis is unduly prolonged, it is convenient to use a current density of about 1 ampere per sq. dm., and to pass more than the theoretical current. The conditions for the electrolysis may be summarised as follows. For the electrolysis of

Sodium benzyl thiosulphate, a concentrated aqueous solution (5 grams in 50 c.c. of water) is used in which an equivalent quantity of sodium carbonate (3.16 grams) has been dissolved. The mixture is warmed to 60–70° and 50 per cent. more than the theoretical current (theory 4.023 ampere-hour) is passed, using a cathode current density of approximately 1 ampere per sq. dm. The disulphide is collected and recrystallised once from alcohol, a pure product being then obtained.

*Butyl disulphide* may be prepared in a similar manner from sodium ethyl thiosulphate, but, being a liquid, it is extracted with ether and purified by distillation.

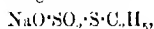
Since the isolation of the pure sodium benzyl thiosulphate is a somewhat tedious process, experiments were next carried out to find whether the mixture obtained by heating together the alcoholic solution of benzyl chloride and aqueous sodium thiosulphate could be directly electrolysed with good results. Since the mixture contains sodium chloride together with sodium benzyl thiosulphate, it was necessary to use a divided cell for the electrolysis, otherwise the chlorine liberated at the anode might enter into reaction with other substances in solution; the anode solution was sodium carbonate. The results were quite satisfactory, a yield of more than 80 per cent. being obtained, especially when the solution was kept well stirred by continuous rotation of the cathode.

Butyl disulphide may be also prepared by the electrolysis of the mixture obtained from the interaction of ethyl iodide and sodium thiosulphate. A yield of about 50 per cent. was obtained. Only one such experiment was carried out, a rotating cathode being used, and the conditions necessary for obtaining a good yield were not further

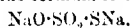
investigated. It is noteworthy that, although in this case the disulphide is a liquid and remains in solution (which contains also to some extent, there does not seem to be any appreciable formation of mercaptan. The disulphide, as it is produced, remains distributed throughout the liquid in the form of fine drops, owing to the action of the rotating cathode, but it does not seem to be reduced, whereas *p*-toluenesulphonyl chloride is reduced to the mercaptan under similar conditions.

At present, no further experiments have been carried out to find under what conditions disulphides may be reduced to mercaptans, but we have confined our attention to the formation of disulphides. It is possible that further investigations on the velocity of reduction of sodium benzyl thiosulphate under known cathode potentials may lead to interesting results.

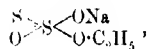
The formation of disulphides by electrolysis throws light on the constitution of thiosulphates. Bunte in his original communication on sodium ethyl thiosulphate (*Ber.*, 1874, **7**, 646) pointed out that the formation of ethyl mercaptan by the decomposition of sodium ethyl thiosulphate by acids was in agreement with the formula :



from which it follows that the formula of sodium thiosulphate is

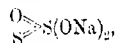


This is also supported by the results of the electrolytic reduction of the salt, since it is difficult to imagine how a disulphide could result from the electrolytic reduction of a compound having the formula :

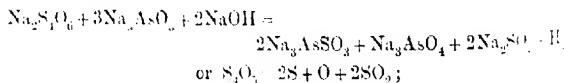


which is deduced from the alternative formula  $\text{S} \begin{smallmatrix} \nearrow \text{ONa} \\ \searrow \text{ONa} \end{smallmatrix}$  for sodium thiosulphate.

Gutmann (*Ber.*, 1905, **38**, 1728 and 327; 1906, **39**, 509; 1907, **40**, 3614), from a study of the action of sodium arsenite (and potassium cyanide) on tri- and tetra-thionates, arrives at the conclusion that the formula for sodium thiosulphate is

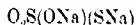


His reasons are as follows. When sodium tetrathionate reacts with sodium arsenite in alkaline solutions, the reaction takes place according to the equation :

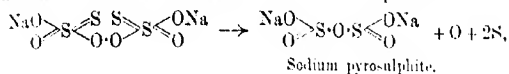


two molecules of monosulphoxyarsenate, one of arsenate, and two of sulphite being formed. According to Gutmann, this could

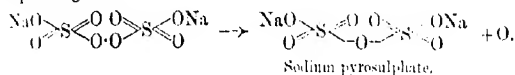
is explained by Mendeléeff's formula for tetrathionate, namely,  $\text{Na}_2\text{O}\cdot\text{SO}_2\cdot\text{S}\cdot\text{S}\cdot\text{SO}_2\cdot\text{ONa}$ , which is derived from the formula :



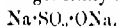
for sodium thiosulphate. If, however, thiosulphate is given the formula  $\text{O}_2\text{S}(\text{ONa})_2$ , the formula for tetrathionate would then be  $\text{NaO}\cdot\text{S}\cdot\text{S}\cdot\text{S}\cdot\text{ONa}$ , that is, a derivative of persulphuric acid. The above reaction could then be explained, thus :



corresponding with



The formula  $\text{O}_2\text{S}(\text{ONa})_2$  is, however, not in accordance with our results, and, moreover, it would lead to the formula  $\text{OS}(\text{ONa})_2$  for sodium sulphite, instead of the generally accepted formula :



The authors are, however, of the opinion that Gutmann's results can be explained by Mendeléeff's formula for sodium tetrathionate.\* Although not explicitly stated, Gutmann's contention seems to be, that the two residues,  $\cdot\text{SO}_2\cdot\text{ONa}$ , which, according to Mendeléeff's formula would be left after the withdrawal of two atoms of sulphur from a molecule of tetrathionate, should unite with the formation of a molecule of dithionate; the dithionate would not then give arsenate and sulphite, since dithionates have no action on arsenites.

Now, Friessner has shown (*Zeitsch. Elektrochem.*, 1904, 10, 265) that dithionate is formed at the anode when neutral or alkaline solutions of sodium sulphite are electrolysed, and that the process is represented by the equation  $2\text{SO}_3'' + \text{O} + \text{H}_2\text{O} = \text{S}_2\text{O}_6'' + 2\text{OH}'$ , and not by the expression  $2\text{SO}_3'' + 2\text{OH}' \rightarrow \text{S}_2\text{O}_6''$ ; that is to say, sulphite ions do not condense directly with the formation of dithionate ions.

The reversal of the first equation would give the two sulphite ions and the one atom of oxygen necessary for the formation of arsenate; two hydroxyl ions (that is,  $2\text{NaOH}$ ) being used up at the same time as required by Gutmann's results. Dithionates, however, are not decomposed by boiling with alkalis, so that the equation does not seem to be reversible; but in the decomposition of tetrathionate, after the

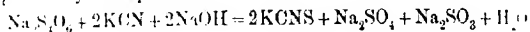
\* The alternative formula of Delars, namely,  $\text{NaO}\cdot\text{SO}_2\cdot\text{S}\cdot\text{O}\cdot\text{SO}_2\cdot\text{SNa}$ , has not been taken into consideration, since Herthoin has shown (*Zeitsch. physikal. Chem.*, 1904, 49, 287) that it does not accord with the experimental facts nearly so well as that of Mendeléeff.

two sulphur atoms are removed, the two residues,  $\text{SO}_2 \cdot \text{ONa}$ , would combine to form dithionate (see above), and would in all probability react according to the equation:



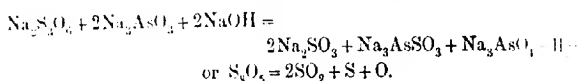
which is in reality the reverse of the above equation. This at the same time probably explains why two molecules of sodium hydroxide are necessary in Gutmann's equation.

A similar explanation will hold for the action of potassium cyanide on sodium tetrathionate. Gutmann found that the reaction was expressed by the equation:



In this case, the free atom of oxygen shown in the equation probably oxidises one of the molecules of sodium sulphite to sodium sulphate.

Gutmann further found that sodium trithionate acts on sodium arsenite in alkaline solution according to the equation:



This also is in accordance with the formula:  $\text{NaO} \cdot \text{SO}_2 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{Na}$  for sodium trithionate.

The latest published results of Gutmann (*Ber.*, 1907, **40**, 361) on the action of alkalis on sodium tetrathionate are explained equally well by Mendeleëff's formula as by that put forward by Gutmann.

#### EXPERIMENTAL.

*Electrolysis of Pure Sodium Benzyl Thiosulphate.*—In these experiments, the current was registered by an ammeter and was maintained constant by means of a variable resistance in the circuit; the time the current passed was measured by a copper coulometer. The solution was stirred from time to time during the electrolysis, and an unalloyed cell was used.

The following table shows the improved yield obtained by the addition of sodium carbonate or bicarbonate. In the first experiment, the pure solution of the substance was electrolysed, whilst in the second and third, equivalent quantities of sodium carbonate and bicarbonate were respectively added. Five grams of sodium benzyl thiosulphate were used in each case, and the volume of the solution was 50 cc. The current is given in terms of that theoretically required for the complete reduction of the substance, and the yields are expressed in percentages of those theoretically expected from the weight of substance taken. The yields were obtained by filtering the crude disulphide into a Gooch crucible, washing well with water, and then

being to constant weight in a vacuum desiccator. The crude disulphide was practically pure, the melting point scarcely altering on recrystallisation. The current density (C.D.) is expressed in amperes per sq. dm.

Current, per cent.	C.D.	Yield, per cent.
107.6	1.27	35.3
106.5	1.27	61.4
97.14	1.27	61.8

The following table shows the effect of variation of (1) the concentration of the solution, (2) the temperature, (3) the current density at the cathode. In each case, 5 grams of the thiosulphate compound were used, and the equivalent quantity of sodium carbonate added.

N.°	Current,* per cent.	C.D.	Volume of solution.	Temp.	Yield, per cent.
1	107.2	1.27	30 c.c.	15°	93.8
2	106.5	1.27	50 "	15	61.4
3	93.4	1.27	100 "	15	42.7
4	107.6	1.27	200 "	15	41.9
5	102.7	1.27	50 "	70	73.5
6	105.2	1.27	50 "	70	81.6
7	100.4	2.54	50 "	15	46.3
8	118.1	56.0	50 "	15	18.0

In each case, the amount of current passed was 100 per cent., according to the ammeter reading, but, since the resistance in the circuit has to be altered from time to time in order to keep the current constant, the correct number of ampere hours was obtained from the ammeter reading, but only from the copper coulometer.

Experiments 1 to 4 show that an increase in the concentration increases the yield, whilst a comparison of 2, 5, and 6 shows the beneficial effect of a higher temperature. The difference in the yield of experiments 5 and 6 is due to the fact that the beaker in the first experiment was covered with a clock glass, thus preventing the liberation of disulphide which took place in experiment 5 with an open beaker.

Experiments 2, 7, and 8 show clearly that a low current density is favorable to the production of the disulphide. This is what might be expected, since with a high current density a large amount of hydrogen would escape, without exerting its reducing action on the complex thiosulphate.

In order to investigate more thoroughly the effect of current density, the actual amount of hydrogen liberated at the cathode was measured, and compared with the amount of hydrogen liberated from a standard (nickel electrodes in a solution of sodium hydroxide) in series with the electrolytic cell. In these experiments, it was, of course, necessary to use a divided cell, each cathode being contained in a separate pot. The apparatus used was similar to that described by Bauer and Schellhaas (*Zeitsch. Elektrochem.*, 1907, 13, 257).

An abstract of the results obtained is given in the following table. The solutions contained one gram of sodium benzyl thiosulphate and one equivalent of sodium carbonate in 40 c.c. The times given are expressed in percentages of the theoretical time necessary for complete reduction. The "per cent. H" signifies the percentage of hydrogen used in reduction.

C.D. = 1.66.		C.D. = 0.655.		C.D. = 0.125.	
Time.	Per cent. H.	Time.	Per cent. H.	Time.	Per cent. H.
7.7	34.8	15.4	57.8	1.4	100.0
39.8	34.6	46.1	48.7	11.2	86.4
53.8	41.1	76.9	43.7	19.7	80.1
76.9	37.7	160.0	40.1	28.1	74.8
166.6	31.7	130.8	30.7	36.5	72.2
124.1	24.8	161.5	23.7	44.9	68.7
146.2	19.0	192.3	13.5	53.4	64.5
162.2	12.1	223.2	13.2	61.8	56.2

A lower current density thus increases the percentage of hydrogen used in reduction. Of the following tables, the first shows that a lead cathode gives slightly better results than one of platinum, the strength of solution being the same as above. The second table shows that an increase in concentration of the solution also gives better results. The solution contained 4 grams of sodium benzyl thiosulphate and an equivalent quantity of sodium carbonate in 40 c.c. of water.

C.D. = 0.125.		C.D. = 0.655.	
Time.	Per cent. H.	Time.	Per cent. H.
1.4	100.0	1.9	86.4
9.8	100.0	9.6	86.4
18.3	88.7	17.4	77.2
26.7	89.7	25.1	72.2
35.1	89.6	32.8	68.7
43.5	81.3	40.5	64.5
52.9	79.7	48.3	64.5
60.4	77.7	56.0	56.2

The crude disulphide obtained with the lead cathode was somewhat discoloured, but one recrystallisation from alcohol gave the pure product. Other experiments showed that the addition of a large excess of sodium carbonate (for example, 5 equivalents) had a retarding effect on the reduction.

A few experiments have been made in which the electrolyte was vigorously stirred (the cathode was stationary). The results given in the following table show that the percentage of hydrogen consumed in reduction decreases slowly at first, since the effect of stirring is continuously to supply fresh portions of the electrolyte to the cathode, but after a time, when most of the compound has been reduced, the percentage of hydrogen used falls rapidly. Only one set of results is given, since indications have been obtained that the previous treatment of the cathode (platinum) must be taken into account, and is of

we have not investigated this. The solution contained one gram of sodium benzyl thiosulphate and one equivalent of sodium carbonate in 100 c.c. C.D. = 2.

Time.	Per cent. H.	Time.	Per cent. H.
5.6	30.9	123.6	30.9
6.4	38.1	174.2	26.0
7.2	39.1	207.9	13.1
7.9	34.0	241.6	8.5
8.9	34.3	269.6	3.7

#### *Electrolysis without Isolating the Sodium Benzyl Thiosulphate.*

As pointed out in the introduction, it was necessary to use a divided cell. In the first experiments, the electrodes were stationary. The method of procedure was as follows. Five grams of benzyl chloride and 100 c.c. of 90 per cent. alcohol were added to a solution of 12 grams of sodium thiosulphate in 20 c.c. of water, and the mixture heated on a water-bath under a reflux condenser for one to one and a half hours. When cold, two equivalents of sodium carbonate\* (11.5 grams) dissolved in 30 c.c. of water were added, and the solution was filtered from the turbidity which formed. The liquid was then electrolysed using a platinum cathode, the anode, being of nickel or platinum, being enclosed in a porous pot or in a parchment tube which contained a strong solution of sodium carbonate. The yields obtained were as follows:

Current, per cent.	C.D.	Temp.	Yield, per cent.
111.7	1.27	Room temp.	53.5
97.8	1.27	" "	59.7
159.4	1.40	" "	86.4
111.8	2.54	69-79	82.3
98.8	1.27	69-79	80.9

The hot solutions thus gave the best yields. The product from the cold solutions was purer, possessing only a faint pink tinge, whilst that from the hot solution had a deeper colour. In both cases, one crystallisation gave the pure product.

In the next experiments, the cathode was rotated during the electrolysis, the anode being in the outer chamber. The inner chamber consisted of a wide glass tube, over the bottom end of which some parchment was securely fastened. The theoretical current as indicated by the ammeter—measurements were not made with a coulometer in these experiments—was passed in each case, the current density being 1.2 amperes per square decm. The temperature was that of the room.

In a divided cell, it is not necessary to add the sodium carbonate to the solution at the cathode, but it is advisable, since the  $\text{CO}_3^{=}$  and  $\text{OH}^-$  ions will carry the current and thus prevent the complex ion  $\text{C}_6\text{H}_5\text{CH}_2\text{S}_2\text{O}_2^-$  from being formed at the anode.



*Experiment 1.*—The solution was not filtered after the addition of a solution of sodium carbonate. The crude product was white, and the yield 86.4 per cent.

*Experiment 2.*—No solution of sodium carbonate was added. The crude product was white, and the yield 79.4 per cent.

Thus a rotating cathode improves the yield, and the addition of sodium carbonate, although not necessary, is advisable.

The pure *dibenzyl disulphide* melted at  $71^{\circ}$ :

0.2222 gave 0.4185  $\text{BaSO}_4$ . S = 25.87.

$(\text{C}_6\text{H}_5\cdot\text{CH}_2)_2\text{S}_2$  requires S = 26.02 per cent.

The *compound* with silver nitrate gave Ag = 26.0;

$(\text{C}_6\text{H}_5)_2\text{S}_2\cdot\text{AgNO}_3$  requires Ag = 26.0 per cent.

#### *Preparation of Diethyl Disulphide.*

(1) Ten grams of sodium ethyl thiosulphate were dissolved in 20 c.c. of water and 1 gram of sodium bicarbonate, dissolved in the same amount of water, added. The solution was electrolysed in a beaker with a platinum wire anode and cathode of platinum foil, 1.4—1.5 cm. (C.D. 1, approx.) being passed for one and a half hours. The *diethyl disulphide* which floated on the surface of the liquid was separated, and the current again passed through the aqueous solution, no more disulphide was formed. The disulphide was then extracted with ether, and the ethereal solution dried over calcium chloride. After removing the ether, a pale yellow liquid was left, which weighed 2.2 grams (a yield of 58 per cent.). On distillation, nearly all the liquid passed over at  $152^{\circ}$ ; the distillate was colourless, and had the properties of *diethyl disulphide*.

(2) Twenty grams of sodium thiosulphate were dissolved in 40 c.c. of water and 10 grams of ethyl iodide, and 40 c.c. of 90 per cent. alcohol added. The mixture was heated on the water-bath for one and a half hours, when a homogeneous solution was obtained. 18.5 Grams of sodium carbonate, dissolved in 40 c.c. of water, were then added to the cold solution, and the mixture electrolysed in a divided cell, using a rotating cathode. The current density was 1 ampere per sq. dm., and five-fourths of the theoretical current was passed. The oil which separated was treated as in (1), and the distillate obtained weighed 1.7 grams (yield = 43 per cent.):

0.2232 gave 0.8456  $\text{BaSO}_4$ . S = 51.9.

$(\text{C}_2\text{H}_5)_2\text{S}_2$  requires S = 52.5 per cent.

0.1763 of the *compound* with silver nitrate gave 0.0651 Ag. Ag = 36.0.

$(\text{C}_2\text{H}_5)_2\text{S}_2\cdot\text{AgNO}_3$  requires Ag = 36.0 per cent.

part of the expense of the foregoing investigations was defrayed by a grant awarded by the Committee of the Research Fund, for which we wish to express our thanks. The research is being continued in various directions.

GENERAL DEPARTMENT,  
MUNICIPAL TECHNICAL SCHOOL,  
BIRMINGHAM.

### XVIII.—*The Double Nitrites of Mercury and the Alkali Metals.*

By PRAFULLA CHANDRA RAY.

On several occasions I have shown that when mercurous nitrite is added with a large volume of water, it undergoes dissociation in accordance with the equation:  $\text{Hg}_2(\text{NO}_2)_2 = \text{Hg} + \text{Hg}(\text{NO}_2)_2$ , and that only 12 per cent. of the salt remains in solution as such, further dilution having no effect (*Zeitsch. anorg. Chem.*, 1896, **12**, 372; *ibid.*, 1897, **71**, 340).

In a paper communicated to the Society about eight years ago I also pointed out that if a sufficient excess of potassium or sodium nitrite or even of silver nitrite is added to this solution, the unchanged portion of mercurous nitrite at once breaks up as above, whilst the alkali nitrite remains unaffected (*Proc.*, 1899, **15**, 103). I was at that time unable to account for this anomalous behaviour.

My more recent work, however, has furnished an explanation. The dissociation of mercurous nitrite ceases as soon as a rather stable compound, mercurous-mercuric nitrite,  $(\text{HgNO}_2)_2 + 4\text{Hg}(\text{NO}_2)_2$ , is formed (*Trans.*, 1902, **81**, 645), and if to this solution an alkali nitrite is added, the latter at once enters into combination with mercuric nitrite, a more stable compound being formed. The mercurous nitrite thus displaced, not being stable in solution in presence of water, at once dissociates; and this process is further accelerated because of the tendency of one of the products of dissociation, namely, mercuric nitrite, to unite with the alkali nitrite. A new method has thus been furnished for the preparation of a series of double salts.

*General Method of Preparation.*—A mixture of mercurous and mercuric nitrite is rubbed to a paste with a minimum quantity of water, water is gradually added, and the undissolved portion filtered off, evaporating the filtrate, which is of a pale yellow colour, over dilute acid under diminished pressure, pale yellow, glistening

tablets and prisms are obtained, which are invariably readily soluble in water. It should be noted here that Lang (*J. pr. Chem.*, [2] **86**, 295) and Rosenheim and Oppenheim (*Zeitsch. anorg. Chem.*, [2] **28**, 171) have already prepared some of the compounds described below by treating mercuric nitrate with concentrated solutions of potassium and sodium nitrites and evaporating the filtrate.

### I. Mercuric Potassium Nitriles.

I have succeeded in preparing two salts of the formula  $\text{Hg}(\text{NO}_2)_2 \cdot 2\text{KNO}_2$  and  $\text{Hg}(\text{NO}_2)_2 \cdot 3\text{KNO}_2 + \text{H}_2\text{O}$  respectively. As will be seen below, mercuric nitrite combines with one, two, three, and even four molecules of the alkali nitrites, the actual number depending on the excess of the latter.

(a)  $\text{Hg}(\text{NO}_2)_2 + 2\text{KNO}_2$ . Analysis gave:

Found (1) Hg = 41.24; K = 16.99; N = 12.16.

" (2) Hg = 40.99\*; K = 17.38.

Theory requires:

Hg = 43.26; K = 16.92; N = 12.12 per cent.

From the mother-liquor of this salt, Rosenheim and Oppenheim prepared another salt of the formula  $\text{Hg}(\text{NO}_2)_2 + \text{KNO}_2$ .

(b)  $\text{Hg}(\text{NO}_2)_2 + 3\text{KNO}_2 + \text{H}_2\text{O}$ . Analysis gave:

Hg = 35.19; K = 20.24; N = 12.00.

Theory requires:

Hg = 35.38; K = 20.75; N = 12.38 per cent.

The peculiarity of this salt is that, although hydrated, it does not give up its water, but retains its lustre intact when kept in a vacuum desiccator over sulphuric acid. Kohnschütter, who has also examined this compound, found that it does not lose water when heated at 100° for a long time (*Ber.*, 1902, **35**, 489).

### II. Mercuric Sodium Nitriles.

(a)  $\text{Hg}(\text{NO}_2)_2 + 1\frac{1}{2}\text{NaNO}_2$ . Analysis gave:

Hg = 50.12; Na = 12.87; N = 8.43.

Theory requires:

Hg = 50.57; Na = 12.39; N = 8.72 per cent.

This compound has not been described by previous workers in this field.

(b)  $\text{Hg}(\text{NO}_2)_2 + 2\text{NaNO}_2 + 2\text{H}_2\text{O}$ . Analysis gave:

Hg = 43.15; Na = 10.40; N = 11.76;  $\text{H}_2\text{O}^+$  = 7.62.

\* The unusually low percentage of mercury is probably due to the salt being contaminated with traces of  $\text{Hg}_2^{++}$ . The water was estimated by the loss on heating.

body requires :

Hg = 42.92 ; Na = 9.87 ; N = 12.02 ; H<sub>2</sub>O = 7.73 per cent.

Ex. 2. is deliquescent.

Oppenheim and Oppenheim, as also Kohlshütter (*loc. cit.*), describe the anhydrous variety of this compound, which I have not been able to prepare. The analysis given above is that of glistening prisms, which did not diminish in lustre even in a vacuum desiccator. The non-efflorescence of this and of the hydrated sodium salt indicate that the water is not loosely combined.

### III. *Mercuric Lithium Nitrites.*

Hg(NO<sub>2</sub>)<sub>2</sub> + 4LiNO<sub>2</sub> + 4H<sub>2</sub>O Analysis gave :

Found (1) Hg = 36.15 ; Li = 4.68,

.. (2) Hg = 34.95 ; Li = 4.76 ; N = 15.08.

body requires :

Hg = 34.72 ; Li = 4.87 ; N = 14.58 per cent.

This salt was obtained as a crystalline mass and is, like other lithium compounds, extremely deliquescent.

From the mother-liquor of the above, a salt of the composition Hg(NO<sub>2</sub>)<sub>2</sub> + LiNO<sub>2</sub> + H<sub>2</sub>O crystallised out. Analysis gave :

Hg = 48.50 ; Li = 2.89 ; N = 13.15.

body requires :

Hg = 48.02 ; Li = 3.37 ; N = 13.46 per cent.

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## XCI. — *Silver-mercuroso-mercuric Oxynitrates and the Isomorphous Replacement of Univalent Mercury by Silver.*

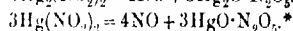
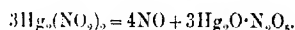
By PRAFULLA CHANDRA RAY.

It has already been shown that the action of silver nitrite on a solution of mercuroso-mercuric nitrite is similar to that of the alkali nitrites with the addition that, not only is mercury separated, but metallic silver is also deposited in shining, minute crystals. There is, however, no evolution of nitrogen nor any change in the radicle NO<sub>2</sub> (Proc., vol. 15, 103).

Owing to the sparing solubility of silver nitrite, my former experiments

were made with boiling solutions. Now, however, the conditions have been somewhat modified. Mercurous and silver nitrites are mixed as a fine paste with the minimum quantity of water, dilution with water being then effected gradually, and the pale yellow filtrate is separated under diminished pressure over sulphuric acid. By this procedure it was expected that a double salt of the type described in the preceding paper would be formed in which the place of the alkali nitrite would be taken by silver nitrite; but lemon-yellow, crystalline precipitates resulted containing both mercurous and mercuric mercury, as well as silver, and the acid radicle was *nitrate* instead of *nitrite*.

Although mercurous-mercuric nitrite is quite stable in solution, it cannot be isolated in the solid state, for when the solution is concentrated by spontaneous evaporation mercurous-mercuric oxyhydrate crystallises out in succession (Trans., 1905, 87, 170). In the present instance, as the reaction takes place in the cold, only a small proportion of mercurous nitrite is replaced by silver nitrite, owing to its slight solubility, and the solution thus contains a mixture of mercurous nitrite and mercurous-mercuric nitrite. During the process of concentration two reactions evidently proceed side by side:



Thus, although silver nitrite is a stable salt and can be crystallised without undergoing decomposition, it is here slowly converted to nitrate owing to the formation of nitric acid. Had there been no silver salt present, the first crop of crystals would have consisted of oxymercurous nitrate,  $\text{HgO} \cdot 2\text{Hg}_2\text{O} \cdot \text{N}_2\text{O}_5$ . A salt of this type was, indeed, formed amongst others, but, as will be shown later, the portion of mercurous mercury was in each case replaced by an equivalent of silver. It is to be regretted that as the salts were in a microcrystalline form, they could not be examined crystallographically.

*Method of Analysis.* The finely-powdered substance was dissolved in the minimum quantity of cold dilute nitric acid. Silver and mercurous mercury were precipitated by the addition of potassium chloride, the mercuric mercury remaining in solution. The precipitate, after careful washing with water, was treated with hydrochloric acid and one or two crystals of potassium chlorate and gently warmed, the solution being then largely diluted with water and set aside until the silver chloride had subsided. The filtrate now represented mercuric mercury, although, of course, oxidised to the mercuric state. Analyses of two different preparations of this typical salt are given below.

\* And possibly also according to the equation  $\text{Hg}(\text{NO}_2)_2 = \text{HgNO}_2 + \text{NO}$  (Trans., 1904, 85, 527).

due to the fact that mercurous chloride is appreciably soluble in ammonium chloride, the mercuric mercury often appears slightly higher:

	Found.	
	Preparation I.	Preparation II.
Mercurous mercury ( $\text{Hg}'$ ) .....	57.89	54.83
Silver .....	6.13	6.77
Mercuric mercury ( $\text{Hg}''$ ) .....	19.50	17.85
Nitrogen .....	2.85	

The ratio ( $\text{Hg}'\text{:Ag}$ ): $\text{Hg}''$ :N in I is approximately 4:1:2.

„ ( $\text{Hg}'\text{:Ag}$ ): $\text{Hg}''$  in II is 4:1.

It should be understood that the ratio of the metals is not invariably 4:1, as is shown by the analyses of two successive crops of another preparation:

	Found.		
	Preparation III.		Preparation IV.
	1st crop.	2nd crop.	
$\text{Hg}'$ .....	58.98	45.81	48.04
Ag .....	7.92	4.15	3.79
$\text{Hg}''$ .....	10.47	26.23	39.67
N .....	5.80	4.04	3.69

The ratios ( $\text{Hg}'\text{:Ag}$ ): $\text{Hg}''$ :N are respectively 7:1:8, 2:1:2, 1.8:1:1.7.

Judging from the distribution of the base and acid, it will be seen that preparations I and II are the most basic, and preparation III the least, whilst that represented by the second crop of preparation III is intermediate between the two.

### Discussion of Results.

The silver and mercurous nitrites were not weighed out in fixed proportions, but simply dissolved together by trituration in a mortar with cold water; hence at the start the components in solution often varied within wide limits. As a result of an extensive investigation of the "conjugated sulphates of the copper-magnesium group" (*Proc. Soc. Edin.*, 1888, 15, 267), it was proved by the author that if the components are dissolved in equivalent proportions and successive crops are collected at intervals, the crystals contain the component sulphates in definite proportions. Thus in the case of copper cobalt potassium sulphate two successive crops had  $\text{Cu}:\text{Co}=5:1$ , whilst in the third crop the ratio was at 1:1 (*loc. cit.*, p. 275). In the case of zinc ammonium sulphate, the first three fractions had the same composition with the ratio of  $\text{Fe}:\text{Zn}=1:3$ ; the next three fractions had the identical composition, only the ratio of the two metals was as 1:1. In short, it was established that the change in composition between two "crops" was not in any sense *continuous*, but distinctly *discontinuous* (*loc. cit.*, p. 281).

In the present instance, it is also evident that within fairly wide

limits in the distribution of the components in solution the ratio  $\text{Hg}'' : (\text{Hg}'\cdot\text{Ag}) = 1 : 4$ , and that in successive crops the change in the ratio of the metals is abrupt and not in slow gradations. Thus, preparation III, whilst the first crop had  $\text{Hg}'' : (\text{Hg}'\cdot\text{Ag}) = 1 : 4$ , the ratio in the second was  $1 : 2$ . In preparation IV, the first crop which was analysed had the ratio of  $\text{Hg}'' : (\text{Hg}'\cdot\text{Ag}) = 1 : 1$ ; but in the second of  $1 : 2$ ; it will be seen that it approached in composition the first crop of preparation III. This apparent anomaly appears to be due to the fact that a salt was actually formed in which  $\text{Hg}'' : (\text{Hg}'\cdot\text{Ag}) = 1 : 2 : 2$ ; but owing to delay in collecting it another salt richer in mercuric mercury had already begun to be deposited. In other words, this is a case of overlapping of two consecutive crops.

It is, of course, well known that in the case of a solution containing isomorphous mixtures the ordinary laws of solubility hold good; the first crop being rich in the least soluble constituent; but as the liquid is to a large extent fractionally removed from the field by the first and second crystallisations, the conditions begin to alter in the third direction, the mother-liquor gradually becoming richer in the more soluble constituent, and this is no doubt the reason why in the first crop of preparation III the proportion of mercurous mercury in the salt  $(\text{Hg}'\cdot\text{Ag})$  diminished. Although in the present series of oxynitrate the ratio between  $\text{Hg}''$  and  $(\text{Hg}'\cdot\text{Ag})$  appears in simple integer ratios, the criterion of isomorphism is equally satisfied. Thus in both preparations I and II, while the ratio of  $\text{Hg}'' : (\text{Hg}'\cdot\text{Ag})$  remains constant the percentage of the different metals varies.\*

A few words on the position of univalent mercury in the periodic system may not be out of place here. Throughout the investigation on mercurous nitrite and hyponitrite, which has been going on during the last twelve years, very marked and striking similarity in properties has been found to obtain between these compounds and the silver analogues (compare *Trans.*, 1897, **71**, 350; *Annalen*, 1898, **316**, 253; *Proc.*, 1907, **23**, 89). The isomorphous replacement of univalent mercury by silver still further emphasises this family likeness. The univalent metals, copper, silver, and gold, have been placed in the first group surrounded by brackets as members of the odd series. Copper and silver isomorphously replace each other in a number of native sulphur compounds as also in the complicated thiocyanates.† But the relationship of these two metals with zinc

\* Compare "Haben die isomorphen Körper die Fähigkeit, miteinander kombinierbare Mischungen zu bilden, in welchen die Mengen der Bestandtheile in einem rationalen Verhältnis zu einander stehen. Diese Eigenschaft bietet auch das beste, ja einzige Kriterium für die Isomorphie."—Dr. Arzruni in *Nachricht. über d. Fortsch. d. Chem.*, Article: "Isomorphie."

† Groth's "Chemical Crystallography," trans. by Marshall, p. 73.

a best very remote. In view of the evidence now adduced, it would appear more rational to substitute mercury for gold and relegate the latter to its more congenial place in the eighth group immediately after platinum. Univalent mercury should be regarded as quite a distinct metal from bivalent mercury; the former is related by ties of closest affinity to silver, whilst the latter is related to members of the second group, namely, magnesium and zinc.\*

From the foregoing investigation, it follows that when a solution containing mercurous-mercuric nitrite and silver mercuric nitrite is allowed to evaporate spontaneously, a series of hydrated silver-mercurous-mercuric oxynitrates crystallises out, in each of which mercurous mercury is isomorphously replaced by silver. It is worthy of note that the present series of compounds are all basic and hydrated.† They retain their lustre untarnished, and do not lose water over sulphuric acid in a vacuum; they give up water, however, readily when heated. It would appear that the predominant partner, bivalent mercury, impresses its own characteristics upon silver, and silver as a rule does not form basic or hydrated salts (compare *ay. Zeitsch. anorg. Chem.*, 1896, 12, 374).

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### C. *The Constituents of the Essential Oil of Nutmeg.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

ALTHOUGH the essential oil distilled from the nutmeg has been known for more than three centuries, and, being recognised by several national pharmacopœias, has long been an established article of commerce, it is a remarkable fact that up to the present time very little of a definite character has been ascertained respecting the nature of its constituents. Previous investigations pertaining to this subject have been recorded by Gildemeister and Hoffmann in their work entitled *Die ätherischen Oele*, Berlin, 1899, p. 474, and also by Semmler in his more recent work, *Die ätherischen Oele*, Leipzig, 1906, Bd. I, pp. 11, 314; III, 211; IV, 165. The correct interpretation of

\* On the twofold position of mercury in the periodic system. See also *Trans.*, 1897, 87, 183. In this respect, mercury is comparable to thallium, which with its trivalent valency affords a remarkable instance of variation of chemical nature.

† The researches of Sâle and recently of Watson have also conclusively proved the existence of silver mercurous peroxynitrates (*Trans.*, 1906, 89, 578).



the results of the earlier investigations is, however, rendered somewhat difficult by the fact that the essential oil of nutmeg has frequently been designated as oil of mace (compare *Pharmacopœia Germanica*, 4th Edition, p. 269), and that the source or genuineness of the oil employed has not always been clearly indicated. It is, indeed, generally assumed that the oils of nutmeg and mace are qualitatively identical, and that they differ only in the relative proportions of their constituents, but, inasmuch as neither of these oils has hitherto been completely examined, there is no direct evidence that this is the case.

Among the more important of the earlier investigations of oil of nutmeg, those of Gladstone may be considered. In his first communication on this subject (*Journ. Chem. Soc.*, 1864, 17, 11), he recorded the following observations. "The three specimens examined consisted of varying proportions of a hydrocarbon resembling carvene, and an oxidised oil with the boiling point  $224^{\circ}$ , and sp. gr. 0.9466. As it closely resembles carvol and menthol in its properties, it may by analogy be named myristicol." In a later communication (*Journ. Chem. Soc.*, 1872, 25, 3, 11), Gladstone suggested for the above-mentioned hydrocarbon the name "myristicene," and remarked further regarding "myristicol" as follows: "This oil has the characteristic smell of nutmeg, and . . . does not form a crystalline compound with hydrosulphuric acid. It was found difficult to purify it by fractional distillation, indeed there was some reason to think that in the process of rectification it was subject to change. An ultimate analysis of portions boiling at somewhere about  $220^{\circ}$  yielded rather too much carbon and hydrogen for the formula  $C_{10}H_{11}O$ , suggesting the idea of its being still mixed with some amount of a hydrocarbon."

The constituents of nutmeg oil were next investigated by C. R. Wright (*Journ. Chem. Soc.*, 1873, 26, 549), who obtained "a considerable quantity of a mixture of hydrocarbons boiling below  $180^{\circ}$  and a small quantity of an oxidised constituent boiling above  $210^{\circ}$ , apparently the 'myristicol' of Gladstone." He noted that the purest myristicol boiled at  $212-218^{\circ}$ , and from an analysis of this fraction concluded that it contained as its principal constituent a body isomeric with camphor,  $C_{10}H_{15}O$ , but as he obtained from it, by repeated distillation, a portion boiling at  $250-265^{\circ}$ , which was assumed to be a polymerised product, the conclusion respecting the composition of the fraction was evidently not justified. With regard to the hydrocarbons, Wright stated that, "contrary to Gladstone's experience, the hydrocarbon of oil of nutmeg is not a single body boiling at  $163-164^{\circ}$  and of formula  $C_{10}H_{16}$ , but a mixture of a terpene boiling at  $163-164^{\circ}$  and a hydrocarbon, apparently cymene, boiling towards  $177^{\circ}$ ." As cymene, however, was only isolated after treating the mixture

sulphuric acid, no evidence was afforded of its pre-existence in the oil.

Brühl (*Ber.*, 1888, 21, 473), with consideration of the statements respecting the character of the so-called "myristicol," and from purely physical data, which apparently were obtained by the examination of a fraction of nutmeg oil boiling at  $224^{\circ}$ , was led to the conclusion that, as an alcohol of the formula  $C_{10}H_{18}O$ , myristicol was to be regarded as a cyclic compound containing two ethylenic linkings. He, moreover, suggested constitutional formulae which were believed to be in accordance with the physical determinations.

Wallach (*Annalen*, 1889, 252, 105) examined the lower boiling portions of an oil which he designated as "mace oil," and positively established the presence of pinene and dipentene. In this connexion, he noted that "it was remarkable that the fractions containing pinene were nearly inactive (very slightly levorotatory). The crude oil, on the other hand, as also the fractions of higher boiling point, were strongly dextrorotatory. It is to be assumed that in the low boiling portion, + and - pinene neutralise each other. The nature of the higher boiling, dextrorotatory portions of mace oil still remains to be cleared up."

The investigation of the oils of nutmeg and mace was subsequently undertaken by Semmler (*Ber.*, 1890, 23, 1803; 1891, 24, 3818). The oil of nutmeg supplied to him had a density of 0.8611 at  $15^{\circ}$ , and was found to consist entirely of terpenes, but these were not further examined. He particularly noted the absence of cymene, "myristicol," and higher boiling oils of high specific gravity, and stated that the oil in question evidently represented the portions which are most volatile in steam. These results led Semmler to examine an oil of mace, which was found to have a specific gravity of 0.9309 at  $14^{\circ}$ , and to give a green coloration with ferric chloride, indicating the presence of a phenolic substance. A fraction collected between  $70^{\circ}$  and  $144^{\circ}$  at 0 mm. pressure was assumed to contain "myristicol," but was not further examined. From the higher boiling portions of the oil, after treatment with sodium, a crystalline substance was isolated, to which Semmler gave the name myristicin, and assigned to it the formula  $C_{11}H_{18}O_3$ . It was subsequently shown, however, that myristicin has the formula  $C_{11}H_{18}O_3$ , and is 3-methoxy-4:5-methylenedioxy-1-allylbenzene. This substance is a liquid, but, by treatment with metallic sodium or with alkalis, it is readily converted into the corresponding propenyl compound (n. p. 45), which has been designated myristicin (compare Thoms, *Ber.*, 1903, 36, 3446; Richter, *Ber. uel. pharm. Ges.*, 1907, 17, 152; Rimini, *Gazzetta*, 34, ii, 281; 35, 406; Rimini and Olivari, *Atti R. Accad. Lincei*, 1907, [v], 16, i, 10).

The purpose of the present investigation has been to ascertain the nature of the constituents of a genuine oil of nutmeg, and especially, among other points of interest, to determine the character of the so-called "myristicol." In addition to the statements already regarding the occurrence of this compound in oil of nutmeg, Wright (*Journ. Chem. Soc.*, 1873, 26, 552) believed it to be also present in very small amount in the oil of sweet orange. He noted that "the portion passing over at 210–230° appeared to be identical with myristol, as it gave numbers agreeing with the formula  $C_{10}H_{16}O$ ." More recently, Thoms (*Ber. Deut. pharm. Ges.*, 1904, 14, 27) has indicated that the essential oil distilled from the seed of *Monodora Myristica* Dunal, contains an oxygenated compound of the composition  $C_{10}H_{16}O$ , which he regarded as probably identical with "myristicol." In connexion with these later observations, it is, however, of interest to note that the constituent of oil of sweet orange which Wright had considered to be identical with "myristicol" has been shown by Siegel (*J. pr. Chem.*, 1900, [ii], 62, 531) to be nothing more than a terpene.

#### EXPERIMENTAL.

##### 1. Examination of a Normal Oil of Nutmeg

The oil employed in this investigation was specially distilled for by Messrs. Stafford Allen & Sons, of London, from unlined Ceylon nutmegs of good quality, and our thanks are due to them for the oil with which the operation was conducted. The amount of oil drawn from 24.38 kilograms of nutmegs was 1693 grams, corresponding to a yield of 6.94 per cent. This oil was a nearly colourless, limpid liquid, having a density of 0.8690 at 15°/15°, an optical rotation of +38.4° in a 1-dm. tube, and was soluble in three times its volume of 90 per cent. alcohol.

A determination of the amount of free acids and esters gave the following data: 20 grams of the oil required 2.9 c.c. of an 8 per cent. alcoholic solution of potassium hydroxide to neutralise the free acids, corresponding to an acid value of 0.81. On subsequently adding an excess of the alkali and boiling for half an hour, it was found that 11.2 c.c. of the decinormal solution were required to hydrolyse the esters present, corresponding to an ester value of 345. These esters, if calculated as  $C_{10}H_{17} \cdot C_2H_3O_2$ , would therefore amount to 1.2 per cent.

As a preliminary test for the presence of aldehydes or ketones, 10 grams of the oil were shaken for some time with a saturated solution of sodium bisulphite. No solid compound was formed, but a clear aqueous liquid, after being freed from adhering oil by shaking with ether, gave on treatment with alkali a trace of an oil which possessed

a fragrant odour. The amount of this substance was, however, much too small to permit of its isolation.

*Treatment with Sodium Hydroxide.*—A quantity (1500 grams) of the oil was extracted several times with a 5 per cent. solution of sodium hydroxide, in order to remove the free acids and any phenolic substances present. The combined alkaline liquids and aqueous washings were shaken with ether to remove any adhering oil, and then acidified with sulphuric acid, when an oily liquid separated. This was extracted with ether, and the ethereal liquid shaken a few times with a 10 per cent. solution of sodium carbonate.

#### *Identification of Myristic Acid.*

The liquids resulting from the extraction with sodium carbonate were acidified with sulphuric acid and distilled with steam. The distillate contained no volatile acids, but there remained in the flask a quantity of a solid substance amounting to about 5 grams, which was collected on a filter and washed with water. On crystallisation from alcohol, it yielded a product melting sharply at 54°:

0.1482 gave 0.3990  $\text{CO}_2$  and 0.1690  $\text{H}_2\text{O}$ .  $\text{C} = 73.4$ ;  $\text{H} = 12.7$ .

$\text{C}_{14}\text{H}_{28}\text{O}_2$  requires  $\text{C} = 73.7$ ;  $\text{H} = 12.3$  per cent.

This substance was thus identified as myristic acid.

#### *Identification of Eugenol and isoEugenol.*

The ethereal liquid which had been extracted with a solution of sodium carbonate, as above described, was dried with anhydrous sodium sulphate, and the ether removed. About 3 grams of a dark brown oil were thus obtained, which possessed an intense odour of eugenol and gave with ferric chloride a deep green colour. By distillation under a pressure of 75 mm., it was resolved into the following three fractions: 164—174°; 174—180°; above 180° 75 mm., only a little non-volatile, resinous substance remaining in the flask. These products were then separately benzoylated, when from the first fraction (b. p. 164—174°/75 mm.) a benzoyl derivative was obtained, which, after fractional crystallisation from alcohol, separated in thick prisms, melting at 67—69°:

0.1765 gave 0.4760  $\text{CO}_2$  and 0.0955  $\text{H}_2\text{O}$ .  $\text{C} = 76.1$ ;  $\text{H} = 6.2$ .

$\text{C}_{17}\text{H}_{18}\text{O}_3$  requires  $\text{C} = 76.1$ ;  $\text{H} = 6.0$  per cent.

The substance yielding this compound was thus identified as eugenol.

The second fraction (b. p. 174—180°/75 mm.) yielded a mixture of benzoyl derivatives, for, when crystallised from alcohol, the first crop of crystals melted somewhat indefinitely between 68° and 84°. After

repeated fractional crystallization, this product melted at 90–100° and was then analysed:

0.1500 gave 0.4158 CO<sub>2</sub> and 0.0851 H<sub>2</sub>O. C = 75.6; H = 6.3.

0.1385 „ 0.3862 CO<sub>2</sub> „ 0.0776 H<sub>2</sub>O. C = 76.0; H = 6.2.

C<sub>17</sub>H<sub>16</sub>O<sub>3</sub> requires C = 76.1; H = 6.0 per cent.

From the melting point and analysis of this compound, it is evident that it was nearly pure benzoylisoegenol, which is stated to melt at 103–104°. The identification of isoegenol as a constituent of nutmeg oil is of considerable interest, inasmuch as hitherto but one instance appears to have been recorded of its occurrence in an essential oil (compare Semmler, "Die ätherischen Öle," Bd. IV, p. 130). The fraction of the phenols boiling above 180°/75 mm. yielded no solid benzoyl derivative.

#### *Preliminary Examination of the Terpenes.*

The oil from which the myristic acid and phenols had been removed, as above described, was washed with water, dried with anhydrous sodium sulphate, and distilled under a pressure of 60 mm. The portion boiling below 110°/60 mm., which would contain practically all the terpenes, was separately collected, and amounted to about 87 per cent. of the entire oil. This portion was subsequently subjected to several fractionations under a pressure of 20 mm., and a fraction boiling below 70°/20 mm. was collected. The density of the latter was found to be 0.8526 at 15°/15°, which proved the absence of any appreciable amount of an olefinic terpene. A portion of the oil which distilled at 170–172° under the ordinary pressure was specially tested for phellandrene, but with a negative result. The further examination of the terpenes was conducted after the hydrolysis of the higher boiling portions of the oil.

#### *Hydrolysis of the Oil.*

The portion of oil collected below 110°/60 mm., as also that boiling above this temperature, was distilled under the ordinary pressure, and the fraction passing over below 190° was collected.

The entire amount of oil boiling above 190° under the ordinary pressure was heated for an hour with an alcoholic solution of 10 grams of potassium hydroxide in a flask provided with a reflux condenser. After distilling off the greater part of the alcohol, water was added and the mixture extracted with ether. The ethereal liquid was washed, dried, and the ether removed, after which the hydrolysed oil was distilled under 15 mm. pressure in order to remove any re-

volatile, resinous matter. The strongly alkaline, aqueous liquid, which remained in the flask after the extraction of the hydrolysed oil, was reserved for the examination of the acids.

#### Fractional Distillation of the Oil.

The hydrolysed oil, together with the portion boiling below  $190^{\circ}$ , which had previously been separated, was next submitted to a systematic fractional distillation at the ordinary pressure, a Young's rod and disc column having been used up to a temperature of  $205^{\circ}$ . The following fractions were ultimately obtained :

Boiling-point.	$d_{20}^{20^{\circ}}$ .	$n_D^{20}$ in a 1 dm. tube.	Amount in grams.
156—159°	0.8519	+ 31.36'	138.0
159—161	0.8513	+ 45.15	351.0
161—163	0.8515	+ 52.10	229.0
163—165	0.8516	+ 18.48	135.0
165—170	0.8514	+ 35.46	29.0
170—180	0.8521	+ 9.1	77.0
180—195	0.8754	+ 1.21	22.0
195—205	0.9119	+ 10.10	9.2
205—215	0.9351	+ 12.41	19.5
215—225	0.9504	+ 9.12	18.0
225—235	0.9656	+ 5.21	8.1
235—245	0.9812	+ 4.12	6.8
245—255	0.9931	+ 5.20	10.2
255—265	1.0166	+ 5.20	17.1
265—275	1.0136	+ 5.10	21.2
Above 275	1.0510	+ 2.25	5.0

Total ... 1667.1 grams.

#### Identification of Pinene.

*Fraction 156—159°.*—This was a colourless, limpid liquid, which possessed the odour of pinene :

0.1018 gave 0.3282  $\text{CO}_2$  and 0.1100  $\text{H}_2\text{O}$ .  $\text{C} = 87.9$  ;  $\text{H} = 12.0$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$  ;  $\text{H} = 11.8$  per cent.

It is evident that this fraction consisted entirely of a hydrocarbon. The presence of pinene was determined by the formation of a crystalline nitrosochloride (m. p.  $108^{\circ}$ ), and the conversion of the latter into the corresponding nitrolbenzylamine (m. p.  $123^{\circ}$ ).

*Fraction 159—161°.*—This was the largest fraction obtained, and it resembled in its characters the preceding one :

0.0658 gave 0.3100  $\text{CO}_2$  and 0.1034  $\text{H}_2\text{O}$ .  $\text{C} = 88.3$  ;  $\text{H} = 12.0$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$  ;  $\text{H} = 11.8$  per cent.

It was found to contain a considerable quantity of pinene, since it readily yielded the above-mentioned derivatives of this terpene.

*Identification of Camphene.*

*Fraction 161—163°.*—This was a large fraction, and resembled in odour the preceding one:

0.1441 gave 0.4650  $\text{CO}_2$  and 0.1555  $\text{H}_2\text{O}$ .  $\text{C} = 88.0$ ;  $\text{H} = 12.0$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

The high optical rotation of this fraction suggested the presence of a considerable amount of camphene. Fifty grams of the liquid were therefore treated with a mixture of acetic and sulphuric acids according to the method of Bertram and Walbaum for the conversion of camphene into an isoborneol ester. After hydrolysing the product, a pale yellow oil was obtained, which was distilled under diminished pressure. A portion which passed over at  $120\text{--}140^\circ/25$  mm. partially solidified in the receiver, and possessed a pronounced camphene-like odour. On treating this fraction with phenylisocyanate in a sealed tube at  $100^\circ$  for several hours, a phenylurethane was obtained, which crystallised from alcohol in fine needles melting at  $138^\circ$ . The latter compound, on treatment with alcoholic potash, yielded a substance which, after crystallising from methyl alcohol, melted at  $207\text{--}210^\circ$ , and had all the characteristic properties of isoborneol. The presence of camphene in this fraction of the oil was thus established.

*Fractions 163—165° and 165—170°.*—These fractions were similar in their general characters to the preceding one, but had a somewhat lower rotatory power. The fraction  $165\text{--}170^\circ$  was analysed:

0.1062 gave 0.3430  $\text{CO}_2$  and 0.1150  $\text{H}_2\text{O}$ .  $\text{C} = 88.1$ ;  $\text{H} = 12.0$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

It was evident that these two fractions consisted of mixtures of pinene and camphene with the constituents of the succeeding fraction.

*Identification of Dipentene.*

*Fraction 170—180°.*—This was a limpid, colourless liquid, possessing a distinctly lemon-like odour:

0.1171 gave 0.3778  $\text{CO}_2$  and 0.1244  $\text{H}_2\text{O}$ .  $\text{C} = 88.0$ ;  $\text{H} = 11.8$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.2$ ;  $\text{H} = 11.8$  per cent.

The analysis of this fraction showed that it contained no oxygenated substances, such as cineol (b. p.  $176^\circ$ ). The fraction readily yielded a bromo-derivative, which, after crystallisation from ethyl acetate, melted at  $124\text{--}125^\circ$ , thus establishing the presence of dipentene. No terpinene could be detected in it.

*Fraction 180—195°.*—This was a colourless liquid, possessing a somewhat lemon-like odour:

0.1567 gave 0.4867  $\text{CO}_2$  and 0.1650  $\text{H}_2\text{O}$ .  $\text{C} = 84.7$ ;  $\text{H} = 11.7$ .

The characters of this fraction indicated it to consist of a mixture of the constituents of the preceding and succeeding ones.

*Identification of Linalool.*

*Fraction 195—205°.*—This fraction possessed a pronounced odour of linalool:

0.1145 gave 0.3352  $\text{CO}_2$  and 0.1191  $\text{H}_2\text{O}$ .  $\text{C} = 79.8$ ;  $\text{H} = 11.6$ .

$\text{C}_{10}\text{H}_{18}\text{O}$  requires  $\text{C} = 77.9$ ;  $\text{H} = 11.7$  per cent.

Although this fraction still contained some terpene, it evidently consisted largely of an oxygenated substance. A portion of it was gently oxidised with a chromic acid mixture and the product extracted with ether. The ethereal liquid was washed, dried, and the ether removed, when a small amount of a product was obtained, which, on distillation, yielded a fraction possessing an intense lemon-like odour. The latter fraction, on treatment with  $\beta$  naphthylamine and pyruvic acid, yielded the crystalline  $\alpha$ -citryl- $\beta$ -naphthacinehonic acid, melting at  $290^\circ$ . This result, together with the positive rotation of the original fraction, rendered it evident that *d*-linalool was present in the oil.

No semicarbazone, oxime, or solid bisulphite compound could be obtained from the above fraction, thus indicating the absence of aldehydes or ketones.

The subsequent fractions of the oil, as previously noted, were all relatively small in amount, but they were analysed with the following results:

*Fraction 205—215°.*

0.1193 gave 0.3441  $\text{CO}_2$  and 0.1210  $\text{H}_2\text{O}$ .  $\text{C} = 78.7$ ;  $\text{H} = 11.3$ .

*Fraction 215—225°.*

0.1684 gave 0.4855  $\text{CO}_2$  and 0.1634  $\text{H}_2\text{O}$ .  $\text{C} = 78.6$ ;  $\text{H} = 10.8$ .

*Fraction 225—235°.*

0.1691 gave 0.4893  $\text{CO}_2$  and 0.1526  $\text{H}_2\text{O}$ .  $\text{C} = 78.9$ ;  $\text{H} = 10.0$ .

*Fraction 235—245°.*

0.1359 gave 0.3930  $\text{CO}_2$  and 0.1191  $\text{H}_2\text{O}$ .  $\text{C} = 78.9$ ;  $\text{H} = 9.7$ .

*Fraction 245—255°.*

0.2367 gave 0.6796  $\text{CO}_2$  and 0.2026  $\text{H}_2\text{O}$ .  $\text{C} = 78.3$ ;  $\text{H} = 9.5$ .

*Fraction 255—265°.*

0.1435 gave 0.4049  $\text{CO}_2$  and 0.1139  $\text{H}_2\text{O}$ .  $\text{C} = 77.0$ ;  $\text{H} = 8.8$ .

*Fraction 265—275°.*

0.1855 gave 0.5090  $\text{CO}_2$  and 0.1386  $\text{H}_2\text{O}$ .  $\text{C} = 74.8$ ;  $\text{H} = 8.3$ .

*Fraction above 275°.*—The amount of this fraction was only 5 grams and, being obviously of an indefinite character, it was not analysed.



The fractions collected between  $195^{\circ}$  and  $245^{\circ}$  were all fragrant liquids, whereas the odour of those obtained between  $245^{\circ}$  and  $275^{\circ}$  was not so distinctive.

As all the fractions which distilled above  $195^{\circ}$  under ordinary pressure were too small in amount to admit of a satisfactory examination, the nature of the oxygenated constituents of the oil was more fully determined by means of a larger quantity of material, designated as heavy oil of nutmeg, which was kindly supplied to us by Messrs. Stafford Allen & Sons. The identification of these constituents will therefore be described in connexion with the examination of the so-called "heavy oil of nutmeg" in the second section of this paper. It may here be noted, however, that among the above fractions those boiling at  $255\text{--}265^{\circ}$  and  $265\text{--}275^{\circ}$  respectively contained a considerable amount of myristicin, for they both readily yielded the dibromo-myristicin dibromide, which crystallised in silky needles melting at  $128\text{--}129^{\circ}$  (*loc. cit.*, 1903, 36, 3446).

#### *Acids Obtained by the Hydrolysis of the Oil.*

The alkaline, aqueous liquid obtained by the hydrolysis of the oil, as previously described, was acidified with sulphuric acid and distilled with steam. The distillate contained some oily drops, and towards the end of the operation a small amount of solid passed over. It was therefore extracted with ether, the ethereal liquid washed with water, dried with anhydrous sodium sulphate, and the ether removed. About 1 gram of a dark brown, oily product was thus obtained, which was converted into a sodium salt, and from the latter five fractions of silver salts were prepared. These were washed, dried in a vacuum over sulphuric acid, and analysed:

Fraction	I.	0.1475 of silver salt gave	0.0459 Ag.	Ag = 31.1.
"	II.	0.1107 " " "	0.0366 Ag.	Ag = 33.1.
"	III.	0.1213 " " "	0.0534 Ag.	Ag = 44.0.
"	IV.	0.1601 " " "	0.0815 Ag.	Ag = 50.9.
"	V.	0.1583 " " "	0.0950 Ag.	Ag = 60.0.

It is evident from these results that the acids extracted by ether represented a rather complex mixture, apparently containing some myristic acid, since silver myristate requires Ag = 32.2 per cent. Their nature was, however, more fully ascertained by the subsequent examination of the corresponding product from "heavy oil of nutmeg."

The aqueous distillate, which had been extracted with ether as above-described, still contained some acid, which was converted into a barium salt. The hot solution of the latter, on cooling, deposited a quantity (about 2 grams) of a salt in glistening leaflets. The

was collected, washed with a little water, dried at  $110^{\circ}$ , and analysed:

0.8233 of the dried salt gave 0.8135  $\text{BaSO}_4$ . Ba = 53.5.

$(\text{C}_9\text{H}_9\text{O}_2)_2\text{Ba}$  requires Ba = 53.7 per cent.

By the evaporation of the mother liquors, a further quantity of a salt was obtained, the solution of which abundantly reduced mercuric chloride on heating. It was likewise dried at  $110^{\circ}$  and analysed:

1.4219 of the dried salt gave 1.4201  $\text{BaSO}_4$ . Ba = 58.7.

$(\text{CHO}_2)_2\text{Ba}$  requires Ba = 60.4 per cent.

These results established the presence of esters of both formic and acetic acid in the oil.

The contents of the distillation flask, after the removal of the volatile acids by steam, were extracted with ether, but only a little resinous matter was obtained.

#### II.—Examination of a Heavy Oil of Nutmeg.

This oil, which, as previously stated, had been kindly supplied to us by Messrs. Stafford Allen & Sons, represented a product obtained by the rectification of very large quantities of normal oil of nutmeg, and consisted chiefly of the oxygenated constituents of the latter, the terpenes having been to a large extent removed. It was a pale yellow liquid, possessing the following constants:  $d_{20}^{20} = 1.102$ ;  $n_D^{17} = 1.4717$  in a 1-dm. tube; saponification value 6.10.

*Treatment with Sodium Hydroxide.*—A quantity (6800 grams) of the oil was extracted several times with a 5 per cent. solution of sodium hydroxide. The combined alkaline liquids and washings were shaken with ether to remove any adhering oil, acidified with sulphuric acid, and the liberated acids and phenols extracted with ether. In order to remove the acids, the ethereal liquid was shaken with a 10 per cent. solution of sodium carbonate. The liquid obtained by extraction with the last-mentioned alkali, when acidified with sulphuric acid and distilled, yielded, however, only traces of acetic and butyric acids. No crystalline acid could subsequently be isolated from the contents of the distilling flask, and therefore the heavy oil, unlike the normal oil of nutmeg, did not contain any free myristic acid.

#### Identification of Eugenol and isoEugenol.

The above-mentioned ethereal liquid, from which the traces of acid had been extracted, was washed with water, dried with anhydrous sodium sulphate, and the ether removed. About 100 grams of crude

phenols were thus obtained, which were first distilled under diminished pressure to remove resinous matter, and then under the ordinary pressure, when the following fractions were collected: 245—250°; 250—260°; above 260°.

*Fraction 245—250°.*—This amounted to about 50 grams, and evidently consisted chiefly of eugenol. Its identity was confirmed by the formation of benzoyleugenol (m. p. 69°), and also of the diphenylurethane, melting at 107—108° (*Ber.*, 1907, 40, 1834).

*Fraction 250—260°.*—This amounted to 25 grams. In attempting to prepare from it a diphenylurethane, it was found that the product did not solidify so readily as in the case of the preceding fraction, and was obviously a mixture. With consideration of the probable presence of isoeugenol, and as the *diphenylurethane* of the latter had not hitherto been prepared, a little of this derivative was made from pure isoeugenol (Kahlbaum) and found to melt at 112—113°, which is but a few degrees higher than the melting point of the corresponding derivative of eugenol. It was thus evident that the diphenylurethanes are well adapted for the differentiation of the above-mentioned isomeric phenols.

*Fraction above 260°.*—This amounted to about 10 grams. It readily yielded a crystalline benzoyl derivative melting at 105°, thus confirming the observation recorded in connexion with the normal oil of nutmeg, that the phenols consist of a mixture of eugenol and isoeugenol.

#### *Hydrolysis of the Oil.*

After the removal of the phenols by extraction with a solution of sodium hydroxide, as above described, the oil was heated with an alcoholic solution of potassium hydroxide (1 part KOH to 100 parts of oil). The greater part of the alcohol was then removed, water added and the separated oil collected, washed, and dried; the aqueous alkaline liquid being reserved for the subsequent examination of the acids.

#### *Fractional Distillation of the Hydrolysed Oil.*

The hydrolysed oil was subjected to a systematic fractional distillation, the portions boiling below 265° being finally collected under the ordinary pressure, whilst the remainder of the oil was fractionated under a pressure of 40 mm. The following results were obtained:

Boiling-point.	$d_{20}^{20}$ .	$\alpha_D$ in a 1-cm. tube.	Amount in grams.
Below 195°	—	—	184
195—205	0.9136	+ 11.22°	35
205—215	0.9432	+ 11.31	440
215—225	0.9666	+ 5.5	238
225—235	1.0070	- 0.33	151
235—245	1.0469	- 0.5	82
245—255	1.0729	+ 1.4	74
255—265	1.1014	+ 1.48	182
165—169°, 40 mm.	1.1316	+ 1.8	130
169—171 „	1.1341	+ 0.51	560
171—173 „	1.1437	+ 0.6	3420
Above 173 „	1.1566	$\pm$ 0.0	60
Total ...			5556 grams.

*Fraction below 195°.*—Since this fraction consisted chiefly of terpenes, which had been thoroughly investigated in connexion with the normal oil, it did not require further consideration.

#### *Identification of Linalool.*

*Fraction 195—205°.*—This was a colourless liquid, possessing the fragrant odour characteristic of linalool:

0.9388 gave 0.2881  $\text{CO}_2$  and 0.1046  $\text{H}_2\text{O}$ .  $\text{C} = 79.5$ ;  $\text{H} = 11.8$ .

$\text{C}_{10}\text{H}_{18}\text{O}$  requires  $\text{C} = 77.9$ ;  $\text{H} = 11.7$  per cent.

The analysis of this fraction indicated that it still contained a small amount of terpene. A quantity of it was gently oxidised with a chromic acid mixture, and the product extracted with ether, when, after the removal of the solvent, a small amount of a yellow liquid was obtained, which was distilled under the ordinary pressure. The portion boiling between 215° and 235° possessed an intense odour of citral, and readily yielded  $\alpha$ -citryl- $\beta$ -naphthacinchonic acid, melting at 197°, thus confirming the presence of linalool in the oil.

#### *Identification of Borneol and Terpineol, and Formation of a Diketone,* $\text{C}_{16}\text{H}_{24}\text{O}_2$ .

*Fraction 205—215°.*—This was a very large fraction. It was a colourless liquid, with an odour resembling that of terpineol:

0.1102 gave 0.4015  $\text{CO}_2$  and 0.1445  $\text{H}_2\text{O}$ .  $\text{C} = 77.7$ ;  $\text{H} = 11.4$ .

$\text{C}_{16}\text{H}_{24}\text{O}$  requires  $\text{C} = 77.9$ ;  $\text{H} = 11.7$  per cent.

*Test for Terpineol.*—A portion of the liquid was shaken with a concentrated solution of hydriodic acid (sp. gr. 1.96), when a heavy, dark-coloured oil was formed. This was separated from the aqueous layer, dissolved in ether, and shaken with a dilute solution of sodium bisulphite to remove the free iodine. The ethereal solution was washed, dried with anhydrous sodium sulphate, and the ether removed,

when a thick oil was obtained which solidified in a freezing mixture. This solid was dried on a porous tile and crystallised from light petroleum, from which it separated in colourless prisms, melting at  $80^{\circ}$ . This melting point was identical with that of dipentene dihydriodide,  $C_{10}H_{14}I_2$ , prepared from terpineol (m. p.  $35^{\circ}$ ), and, when the two preparations were intimately mixed, the melting point remained unchanged. It was thus evident that this fraction of the oil contained a considerable amount of terpineol, and its presence was confirmed by the isolation of the ketolactone,  $C_{10}H_{16}O_3$ , from the products of its oxidation.

*Oxidation of the Fraction. Formation of the Ketolactone,  $C_{10}H_{16}O_3$ , a Diketone,  $C_8H_{14}O_2$ , and Camphor.*—A quantity (150 grams) of the fraction (b. p.  $205-215^{\circ}$ ) was oxidised with a chromic acid mixture in the proportions of potassium dichromate (8 parts), sulphuric acid (12 parts), and water (36 parts) to 1 part of oil. In the beginning of the oxidation the odour developed was that of citral, but finally it became distinctly camphoraceous. After the mixture had been gently heated on a water-bath for about an hour, it was allowed to cool, and then extracted several times with ether. The ethereal liquid was first washed with a solution of sodium carbonate to free it from acidic substances, then with water, and the ether removed. A yellow oil was thus obtained, which was distilled with steam, when the greater portion passed over. The non-volatile portion of the oxidation product was extracted by ether, the ethereal solution being washed, dried, and the ether removed. A small quantity of a viscid, brown oil was thus obtained, which deposited no solid, even on long standing. It was finally distilled under diminished pressure, when the fraction of highest boiling point was obtained as a viscid, yellow liquid, which solidified when stirred with light petroleum. This solid was dried on a porous tile and crystallised from ether, from which it separated in colourless prisms melting at  $62-63^{\circ}$ :

0.1165 gave 0.2782  $CO_2$  and 0.0907  $H_2O$ .  $C = 65.1$ ;  $H = 8.7$ .

$C_{10}H_{16}O_3$  requires  $C = 65.2$ ;  $H = 8.7$  per cent.

It is evident that this substance is identical with the ketolactone,  $C_{10}H_{16}O_3$  (m. p.  $64^{\circ}$ ), which was obtained by Wallach by the oxidation of terpineol with chromic acid. As it is the optically inactive modification of the ketolactone, it follows that the terpineol contained in the oil must be the racemic form (compare Wagner and Bricker, *Ber.*, 1899, 32, 2315).

The portion of the above-mentioned oxidation product which was volatile in steam possessed a strongly camphoraceous odour, although no solid substance separated. The distillate was then extracted with ether, the ethereal solution dried, and the solvent removed, when a

quantity of an oily liquid was obtained. One part of this oil, in alcoholic solution, was heated for some time on a water-bath with hydroxylamine hydrochloride (1 part) and sodium hydroxide (1.5 parts), after which water was added and the mixture carefully neutralised with sulphuric acid. As no solid oxime separated, the mixture was extracted with ether, the ethereal solution being washed, dried, and the solvent removed, when a brown oil was obtained which solidified on stirring with light petroleum. This solid substance was collected on a filter and crystallised from hot alcohol, from which, on cooling, it separated in small, rectangular prisms melting at  $140^{\circ}$ . The yield of this compound was about 3 grams:

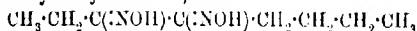
0.1368 gave 0.2804  $\text{CO}_2$  and 0.1187  $\text{H}_2\text{O}$ .  $\text{C} = 55.9$ ;  $\text{H} = 9.6$ .

0.1534 „ 0.3137  $\text{CO}_2$  „ 0.1272  $\text{H}_2\text{O}$ .  $\text{C} = 55.8$ ;  $\text{H} = 9.2$ .

0.1938 „ 27.4 c.c. moist nitrogen at  $16.5^{\circ}$  and 762 mm.  $\text{N} = 16.1$ .

$\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{C} = 55.8$ ;  $\text{H} = 9.3$ ;  $\text{N} = 16.3$  per cent.

From these results, it appears highly probable that this compound is the dioxime of a diketone,  $\text{C}_8\text{H}_{14}\text{O}_2$ . The only known compound of the formula  $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$  with which it might be identical is the dioxime of ethyl butyl diketone,



(m. p.  $139-141^{\circ}$ ), which has been described by Filletti and Ponzio (*J. pr. Chem.*, 1898, [ii], 58, 361). These authors also prepared an osazone, which was found to melt at  $96-97^{\circ}$ . With the object of ascertaining whether our dioxime is identical with that prepared by Filletti and Ponzio, 50 grams of the fraction (b. p.  $205-215^{\circ}$ ) were oxidised as previously described, and the portion of the oxidation product which was volatile in steam treated with an excess of phenylhydrazine in alcoholic solution. No solid osazone could, however, be obtained from the product of the reaction. An attempt was also made to obtain a semicarbazone of the diketone,  $\text{C}_8\text{H}_{14}\text{O}_2$ , from the volatile oxidation product of the fraction  $205-215^{\circ}$ , but without success. These results therefore do not permit of any conclusion respecting the identity of the compound  $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$ , here described, with the dioxime of ethyl butyl diketone prepared by Filletti and Ponzio (*loc. cit.*).

The dioxime,  $\text{C}_8\text{H}_{16}\text{O}_2\text{N}_2$ , is a colourless, odourless substance, sparingly soluble in cold, but readily in hot, alcohol. It is also soluble in warm ethyl acetate, from which it crystallises in fine needles, but is only sparingly soluble in benzene, and insoluble in light petroleum and in water. When warmed with dilute sulphuric acid, it first dissolves, developing a fragrant odour, but, as resinification ensued, it was impossible by this means to regenerate the ketone from which it had been formed.

Since not more than a trace of substance of aldehydic or ketonic nature was present in the fraction of the oil employed, it is evident that the above-mentioned diketone must represent the oxidation product of an unidentified compound, which is doubtless an *alcohol*.

The light petroleum liquid which had been separated from the dioxime, as above described, possessed a strongly camphoraceous odour. After the removal of the solvent, a brown oil was obtained which did not solidify, and was therefore distilled under diminished pressure. From the first portions of the distillate a solid separated which had the characteristic odour of camphor, and, after drying on a porous tile, melted at  $170-175^{\circ}$ . This substance readily yielded a semicarbazone melting at  $238^{\circ}$ , and when the latter was mixed with camphorsemicarbazone the melting point remained unchanged. So, having obtained the camphor in the form of its oxime by the treatment of the original product of oxidation with hydroxylamine, it may be assumed that the amount of the latter was only sufficient to combine with the diketone which was present in the mixture.

The identification of camphor as a product of oxidation of the fraction boiling between  $205^{\circ}$  and  $215^{\circ}$  affords conclusive evidence of the presence of borneol in the original oil.

#### *Identification of Geraniol.*

*Fraction 215–225°.*—This was a comparatively large fraction. It was a colourless liquid, possessing a rose-like odour:

0.1109 gave 0.3136  $\text{CO}_2$  and 0.1055  $\text{H}_2\text{O}$ .  $\text{C} = 77.1$ ;  $\text{H} = 10.6$ .

This fraction was found to contain some terpineol, since it readily yielded the crystalline dipentene dihydride (m. p.  $80^{\circ}$ ) on treatment with concentrated hydriodic acid, whilst the analytical results also indicated it to contain some of the constituents of the succeeding fraction.

A portion of the fraction was oxidised with a chromic acid mixture, when the odour of citral was at first strongly developed, and from the final product a further small amount of the diketone,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , was obtained in the form of its dioxime (m. p.  $140^{\circ}$ ), which has been described in connexion with the preceding fraction.

As the odour of the fraction, together with the evident formation of citral by its limited oxidation, indicated the presence of geraniol, a portion of it was treated with diphenylcarbamic chloride in the presence of pyridine, according to the method suggested by Erdmann (*J. pr. Chem.*, 1897, [ii], 56, 8), when a product was obtained which crystallised from alcohol in thin, colourless needles melting at  $41-42^{\circ}$ . This was found to be identical with the diphenylurethane (m. p.  $42^{\circ}$ ).

prepared from a specimen of pure geraniol, and the presence of the latter compound in the oil was therefore established.

#### *Identification of Safrole.*

*Fraction 225—235°.*—This was a pale yellow liquid, possessing a pleasant odour of safrole, and also the rose-like odour of geraniol :

0.1122 gave 0.3154  $\text{CO}_2$  and 0.0333  $\text{H}_2\text{O}$ .  $\text{C} = 76.2$ ;  $\text{H} = 9.2$ .

The presence of a considerable proportion of geraniol in this fraction was evident from the fact that it yielded the diphenylurethane (m. p.  $52^\circ$ ), and, when gently oxidised, some citral was obtained, which was identified by the formation of the  $\alpha$ -citryl- $\beta$  naphthacinchonic acid, melting at  $195\text{--}197^\circ$ . The odour of the fraction, together with its density and the analytical figures, indicated, however, that it contained safrole.

A portion was oxidised with a mixture consisting of potassium permanganate (8 parts), sulphuric acid (12 parts), and water (30 parts) and 1 part of oil. After heating gently for two hours, a distinct odour of piperonal was observed. The mixture, after being allowed to cool, was repeatedly extracted with ether, the ethereal liquids washed first with water, then with aqueous sodium carbonate, which removed only a trace of acidic substance, finally again with water, and the ether removed. A brown, oily residue was thus obtained, which was shaken with a saturated solution of sodium bisulphite, when a small amount of a solid compound separated. This was collected on a filter by the aid of a pump, and washed with ether. On warming with dilute alkali, a substance was liberated which had the odour of piperonal. This volatile liquid was subsequently extracted with ether, the ethereal liquid being washed, dried, and the ether removed. The residual liquid was placed in a freezing mixture and nucleated with a small quantity of piperonal, when crystallisation ensued, and the resulting product melted at  $34\text{--}35^\circ$ . This was identified as piperonal, thus confirming the presence of safrole in the oil.

The fraction (b. p.  $225\text{--}235^\circ$ ), as well as the two preceding ones, was treated with semicarbazide hydrochloride and sodium acetate in alcohol solution, and the uncombined oil subsequently removed by extraction with steam, when a very small amount of a solid semicarbazone was obtained. On treatment with dilute sulphuric acid, it yielded a few drops of a yellow oil, which possessed an odour resembling that of citral, but gave a  $\beta$ -naphthacinchonic acid derivative which, when crystallised from alcohol, separated in nearly colourless needles melting at  $248^\circ$  with decomposition. The substance, evidently *isobutyrol*, which yielded this derivative was so small in amount that it was impossible further to characterise it.

ANAL.



As this fraction of the oil was slightly levorotatory, it must have contained a small amount of some undetermined substance; piperonal and safrole are optically inactive, and the preceding and the principal succeeding fractions were dextrorotatory.

*Fraction 235—245*.—This was a colourless liquid, possessing a strong odour of safrole:

0.2001 gave 0.5592  $\text{CO}_2$  and 0.1417  $\text{H}_2\text{O}$ .  $\text{C}=75.0$ ;  $\text{H}=7.2$ .

The presence of safrole was proved, as described in connection with the preceding fraction, by the isolation of a small quantity of piperonal, melting at  $33\text{--}35^\circ$ , from the products of its oxidation.

*Fraction 245—255*.—This was a colourless liquid, which was slightly yellow on standing. It was comparatively small in amount:

0.1592 gave 0.4126  $\text{CO}_2$  and 0.1021  $\text{H}_2\text{O}$ .  $\text{C}=74.9$ ;  $\text{H}=7.3$ .

This fraction was specially tested for the methyl ether of safrole, but with a negative result, since it yielded neither the corresponding bromo-derivative nor could any veratric acid be isolated from the products of its oxidation. On oxidation, however, it developed a strong odour of piperonal, indicating the presence of safrole. It yielded on treatment with bromine a compound which crystallized from alcohol in small needles melting sharply at  $128\text{--}129^\circ$ . This was identified as the bromo-derivative of myristicin, which was subsequently described.

*Fraction 255—265*.—This was considerable in amount:

0.1550 gave 0.4048  $\text{CO}_2$  and 0.0984  $\text{H}_2\text{O}$ .  $\text{C}=71.2$ ;  $\text{H}=7.1$ .

It was evident that this fraction consisted largely of myristicin, together with a small amount of some dextrorotatory substance, probably a sesquiterpene, which it was impossible to isolate.

The subsequent fractions, which had been distilled under diminished pressure, were analysed with the following results:

*Fraction 165—169*, 40 mm.

0.1500 gave 0.3854  $\text{CO}_2$  and 0.0956  $\text{H}_2\text{O}$ .  $\text{C}=70.1$ ;  $\text{H}=7.4$ .

*Fraction 169—171*, 40 mm.

0.1737 gave 0.4457  $\text{CO}_2$  and 0.1089  $\text{H}_2\text{O}$ .  $\text{C}=70.0$ ;  $\text{H}=7.6$ .

Each of these fractions evidently consisted chiefly of the combination of the following fraction.

#### *Identification of Myristicin, $\text{C}_{11}\text{H}_{12}\text{O}_3$*

*Fraction 171—173*, 40 mm. —This was by far the largest fraction, the heavy oil of nutmeg, amounting to 3120 grams, or more than half of the total quantity of oil employed. When freshly distilled it was a colourless liquid, possessing only a faintly aromatic odour.

0.1160 gave 0.3728  $\text{CO}_2$  and 0.0844  $\text{H}_2\text{O}$ .  $\text{C} = 69.2$ ;  $\text{H} = 6.4$ .

0.1185 " 0.2875  $\text{CO}_2$  " 0.0677  $\text{H}_2\text{O}$ .  $\text{C} = 69.1$ ;  $\text{H} = 6.6$ .

0.1221 " 0.6098  $\text{CO}_2$  " 0.1400  $\text{H}_2\text{O}$ .  $\text{C} = 68.6$ ;  $\text{H} = 6.4$ .

$\text{C}_{11}\text{H}_{12}\text{O}_3$  requires  $\text{C} = 68.7$ ;  $\text{H} = 6.2$  per cent.

$n_D^{20} = 1.4337$ ;  $n_D^{25} = 1.4066$  in a 1-dm. tube;  $n_D^{20} = 1.54032$ .

The results of analysis and the determination of the physical constants of this fraction rendered it evident that it consisted of nearly pure myristicin. This compound has previously been obtained from a material designated as mace oil (Thoms, *Ber.*, 1903, 36, 3446). The report of its occurrence in oil of nutmeg has hitherto been lacking. *Isobromomyristicin Dibromide*,  $\text{C}_{11}\text{H}_{10}\text{O}_3\text{Br}_4$ .—This was prepared according to the method described by Thoms (*loc. cit.*). When crystallised from a mixture of alcohol and ethyl acetate, it separated in fine, colourless, silky needles, melting at  $128-129^\circ$ :

0.285 gave 0.2000  $\text{CO}_2$  and 0.0402  $\text{H}_2\text{O}$ .  $\text{C} = 25.2$ ;  $\text{H} = 2.1$ .

$\text{C}_{11}\text{H}_{10}\text{O}_3\text{Br}_4$  requires  $\text{C} = 25.9$ ;  $\text{H} = 2.0$  per cent.

Thoms described this compound as a white, crystalline powder, melting at  $130^\circ$ .

*Isomyristicin*.—A quantity (20 grams) of the fraction (b. p.  $173-174/10$  mm.) was heated on a water-bath for two days with an alcoholic solution of 50 grams of potassium hydroxide, and the residue extracted with ether. After the removal of the solvent, it was distilled under diminished pressure, when practically all passed over at  $166-168$  mm. as a colourless, viscid liquid, which, when placed in a freezing mixture, readily solidified. It was crystallised from alcohol from which it separated in radiating clusters of needles, melting at  $44^\circ$ :

0.135 gave 0.3380  $\text{CO}_2$  and 0.0757  $\text{H}_2\text{O}$ .  $\text{C} = 68.5$ ;  $\text{H} = 6.3$ .

$\text{C}_{11}\text{H}_{12}\text{O}_3$  requires  $\text{C} = 68.7$ ;  $\text{H} = 6.2$  per cent.

The refractive index of this substance, kindly determined for us by Dr. Friedrich H. Loes, was  $n_D^{20} = 1.56551$ , whereas that of myristicin at the same temperature was 1.52927.

*Isobromomyristicin Dibromide*.—This was easily prepared by the same method as that employed for the corresponding bromo-derivative of myristicin. When crystallised from a mixture of alcohol and ethyl acetate, it separated in stout needles, melting at  $156^\circ$ :

0.245 gave 0.1915  $\text{CO}_2$  and 0.0406  $\text{H}_2\text{O}$ .  $\text{C} = 25.9$ ;  $\text{H} = 2.2$ .

$\text{C}_{11}\text{H}_{10}\text{O}_3\text{Br}_4$  requires  $\text{C} = 25.9$ ;  $\text{H} = 2.0$  per cent.

#### *Oil Obtained by the Hydrolysis of the Heavy Oil of Nutmeg.*

The alkaline liquid and aqueous washings obtained by the treatment of the oil, as previously described, were concentrated, acidified with sulphuric acid, and distilled with steam. The distillate

contained a quantity of acids in the form of a pale yellow liquid, which was extracted by means of ether. From the aqueous liquid which was still strongly acid, about 20 grams of a barium salt were obtained. This was fractionally crystallised, and each fraction analysed, when it was found to consist entirely of barium salt.

Fraction	I.	0.8950 of the salt gave	0.8106 $\text{BaSO}_4$	$\text{Ba} = 53.7$
"	II.	0.7324	" "	0.7247 $\text{BaSO}_4$ $\text{Ba} = 53.7$
"	III.	0.4997	" "	0.4573 $\text{BaSO}_4$ $\text{Ba} = 53.7$
"	IV.	0.7443	" "	0.6802 $\text{BaSO}_4$ $\text{Ba} = 53.7$
$(\text{C}_{12}\text{H}_{15}\text{O}_2)_2\text{Ba}$ requires $\text{Ba} = 53.7$ per cent.				

The pale yellow, oily acids which had been extracted from the distillate by means of ether, as above described, amounted to 16.6 grams. These were distilled under the ordinary pressure, and at  $270^\circ$ , and the remainder at 20 mm. pressure, when the following fractions were obtained: (a) below  $230^\circ$ ; (b)  $230-250^\circ$ ; (c)  $250-270-290$  mm.; (d)  $190-230/20$  mm. Each of these fractions was converted into a sodium salt, from which, by fractional precipitation with a solution of silver nitrate, a number of salts were prepared. These were washed, dried in a vacuum over sulphuric acid, and analysed:

(a)	0.0882 gave	0.0386 Ag.	Ag = 43.8.
(b)	0.1150 gave	0.0492 Ag.	Ag = 42.8.
	0.1835	" 0.0789 Ag.	Ag = 43.0.
	0.1531	" 0.0661 Ag.	Ag = 43.4.
	0.1752	" 0.0799 Ag.	Ag = 45.1.
(c)	0.1044 gave	0.0434 Ag.	Ag = 41.6.
	0.1862	" 0.0806 Ag.	Ag = 43.3.
	0.1751	" 0.0765 Ag.	Ag = 43.7.
	0.1231	" 0.0544 Ag.	Ag = 44.2.
(d)	0.1272 gave	0.0503 Ag.	Ag = 39.5.
	0.2145	" 0.0856 Ag.	Ag = 39.9.
	0.2309	" 0.0968 Ag.	Ag = 41.9.

$\text{C}_{12}\text{H}_{15}\text{O}_2\text{Ag}$  requires Ag = 43.0 per cent.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{Ag}$  " Ag = 40.8 " "

It would appear from these results that the volatile acids obtained by the hydrolysis of nutmeg oil contain a small proportion of an octoic acid, with smaller amounts of acids of higher and lower molecular weight.

#### *Isolation of a New Monocarboxylic Acid, $\text{C}_{12}\text{H}_{17}\text{O}_2\text{H}$ .*

After the removal of the volatile acids by distillation, which was as above described, there remained in the distillation flask a

11. This was spread on a porous plate, when a quantity of water became absorbed and a crystalline solid was obtained. The water was purified by dissolving it in hot dilute acetic acid, through which it crystallised in hexagonal prisms, melting at  $84-85^{\circ}$ , and possessed a slightly yellow tint. When crystallised from 95 per cent. alcohol, it separated in needles. The substance is extremely soluble in the usual organic solvents, but is insoluble in water:

100 g. gave 0.2972  $\text{CO}_2$  and 0.0861  $\text{H}_2\text{O}$ . C = 70.4; H = 8.3.

100 " " 0.2620  $\text{CO}_2$  " 0.0758  $\text{H}_2\text{O}$ . C = 70.4; H = 8.3.

$\text{C}_{13}\text{H}_{18}\text{O}_3$  requires C=70.3; H=8.1 per cent.

100 g. in alcoholic solution, neutralised 7.4 c.c.  $\text{N}/10$   $\text{NaOH}$ .

$\text{C}_{13}\text{H}_{17}\text{O}\cdot\text{CO}_2\text{H}$  requires 7.4 c.c.

12. A newly known monocarboxylic acid of the formula  $\text{C}_{13}\text{H}_{18}\text{O}_3$  having properties similar to those of the above compound (isobutyropropionic acid, which has been described by Bischoff (1909, 33, 1270) as forming colourless prisms, melting at  $78-79^{\circ}$ ). A specimen of the latter acid was therefore prepared for the purpose of comparison with the above described compound, and the two substances were found to be not identical. The substance isolated from nutmeg oil is therefore to be regarded as a new *isobutyropropionic acid*,  $\text{C}_{13}\text{H}_{17}\text{O}\cdot\text{CO}_2\text{H}$ .

#### Summary.

The results of this investigation have shown that the essential oil of nutmeg contains the following substances:

- |                              |                       |
|------------------------------|-----------------------|
| 1. Alcohol,                  | } about 0.2 per cent. |
| 2. Benzene,                  |                       |
| 3. Ester,                    | } about 80 per cent.  |
| 4. 100 per cent.             |                       |
| 5. Pinene, about 8 per cent. |                       |
| 6. Camphor,                  | } about 6 per cent.   |
| 7. Camphol,                  |                       |
| 8. Camphyl,                  |                       |
| 9. Camphyl,                  |                       |

A new alcohol, yielding on oxidation a diketone,  $\text{C}_8\text{H}_{14}\text{O}_2$ , in very small amount.

A trace of an aldehyde resembling citral, but yielding a *trans-butamic acid* derivative melting at  $248^{\circ}$ .

Stearic acid, about 0.6 per cent.

Myristicin,  $\text{C}_{11}\text{H}_{12}\text{O}_2$ , about 4 per cent.

Myristic acid, in the free state, about 0.3 per cent., and apparently present in the form of esters.

Caproic, acetic, butyric, and octoic acids, and a new *mono-*

*carboxylic acid*,  $C_{13}H_{26}O_2$ , all in the form of esters, and in relatively small amount.

Although the proportions of the above-mentioned constituents, as then indicated for what we have designated a normal oil of *Myrtus*, it is obvious that as the latter differed in its physical character, particularly in its optical rotatory power, from the standards previously adopted for this oil, the composition is subject to considerable variation, according to the character of the material employed for distillation.

This investigation has, furthermore, shown that the present nutmeg oil which has hitherto been designated "myristic," a mixture of alcohols, of which terpineol appears to be the predominant constituent.

In view of the fact that narcotic properties are attributed to *Myrtus* nutmeg, the authors are at present engaged in an investigation of its constituents other than the essential oil.

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# CC]. *The Resolution of sec-Octyl Alcohol (Menthylcarbinol, Octane-2-ol).*

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

THE method described by one of us and W. O. Littlebury (this vol., 1906, 89, 467) for the resolution of racemic alcohols by the fractional crystallisation of an ester of *l*-menthylcarbamie acid fails in the case of *sec*-octyl alcohol, as the ester formed by this alcohol is at once resolved, however, is readily effected by another method, as described by one of us and W. O. Littlebury (this vol., 1906, 89, 467) for the preparation of pure *d*- and *l*-isoborneol.

Phthalic anhydride combines readily with *sec*-octyl alcohol; the resulting acid ester is almost quantitatively resolved by the addition, first of the brucine salt and then of the cinchonidine salt; the acid ester obtained from the more soluble portion of the mixture

The active alcohol is very stable and not readily racemized, the ease with which both optical isomerides can be obtained from this alcohol more convenient than any other for experimental purposes, both the dextro- and levo-forms are required.

It has already been shown by Marekwald and McKenney (this vol., 1904, 34, 469) that commercial *sec*-octyl alcohol, which is the

Castor oil with potash, is a mixture of the inactive compound and some of the levo-alcohol, and that the same can be partially purified by fractional esterification with *D*-tartaric acid. However, the maximum rotation of the product obtained by their method was not greater than  $[\alpha]_D^{20} 1^\circ$ , whereas the pure alcohol has  $[\alpha]_D^{20} 9.8^\circ$ .

We propose shortly to communicate to the Society results of similar experiments carried out with the simpler aliphatic alcohols.

#### EXPERIMENTAL.

The octyl alcohol used in our experiments was Kahlbaum's II purity. In a 2-cm. tube, it gave  $\alpha = 0.15^\circ$ .

*rac*-*sec*-Octyl Hydrogen Phthalate,  $C_{18}H_{32}O_2$  ( $C_8H_{17}$ · $CO_2H$ ).—Equal quantities of *sec*-octyl alcohol and phthalic anhydride are heated at  $110^\circ$ – $120^\circ$  for fifteen hours. An excess of ethyl alcohol is added, and the mixture heated on the water-bath. The mass is dissolved in sodium carbonate solution, which is extracted with light petroleum to remove traces of neutral esters, unchanged alcohol, and soluble impurities of the commercial alcohol. The alkaline solution is acidified, and the acid ester extracted with ether and crystallised from light petroleum. The crystalline mass obtained melts at  $146^\circ$  and is very soluble in benzene, alcohol, chloroform, and either from acetone or acetic acid, from which it may also be readily crystallised.

*rac*-*rac*-*sec*-Octyl Hydrogen Phthalate. —Sixty-five grams of the pure acid ester are dissolved in about 1 litre of acetone and boiled over a reflux condenser with 92 grams of brucine. After the brucine has dissolved, the solution, when cold, deposits clusters of small prismatic crystals of the salt, which melt at  $146^\circ$ – $148^\circ$  and  $[\alpha]_D^{20} = +6.7^\circ$  in ethyl-alcoholic solution. Two recrystallisations from acetone give the pure salt, which melts at  $151^\circ$ . The mother liquor may be worked up and give a further crop of the pure salt, the total yield being about 73 grams. Analysis shows the salt to be composed of 1 molecule of each component (N found 4.4, instead of 4.2 per cent.). The specific rotation of the salt is  $[\alpha]_D^{20} = +5.41^\circ$  in ethyl-alcoholic solution ( $c = 5$ ), and this as well as the melting point is confirmed by six recrystallisations from acetone.

*rac*-*rac*-*tert*-Octyl Hydrogen Phthalate.—The brucine salt is dissolved in a small quantity of alcohol and poured into dilute hydrochloric acid. The phthalated acid ester crystallises very readily from a large quantity of light petroleum in large, stout prisms, which melt at  $146^\circ$ . When titrated, 0.4492 neutralised 0.0644 gram NaOH; theory requires 0.0646 gram. The following polarimetric observations were made in a 2-cm. tube:

0.2617, made up to 20 c.c. with chloroform, gave  $\alpha + 4.13^\circ$ , whence  $[\alpha]_D + 42.94^\circ$ .

1.0150, made up to 20 c.c. with ethyl alcohol, gave  $\alpha + 4.1^\circ$ , whence  $[\alpha]_D + 48.08^\circ$ .

These specific rotations were unaltered by recrystallisation of the substance.

*1-Chinchonidine 1-sec-Octyl Phthalate*.—The mother liquors from the brucine salt are precipitated by hydrochloric acid, and yield a substance which has  $[\alpha]_D - 42.4^\circ$  in ethyl-alcoholic solution. The chinchonidine salt is prepared in a similar manner to the brucine salt. It crystallises from aqueous acetone in long, felted needles, and after recrystallisations melts indefinitely between  $112^\circ$  and  $116^\circ$ , and has a constant rotation:

0.2497, made up to 20 c.c. with ethyl alcohol, gave  $\alpha - 6.46^\circ$ , whence 2 dm. tube, whence  $[\alpha]_D - 68.02^\circ$ .

*1-sec-Octyl hydrogen phthalate* is easily obtained from the chinchonidine salt. It crystallises from light petroleum in lustrous prisms, very similar in appearance to those of the dextro-ester, and melts at  $75^\circ$ . When titrated, 0.4543 neutralised 0.0652 gram NaOH, and requires 0.0653 gram. The specific rotation is practically identical with that of the optical antipode:

0.2963, made up to 20 c.c. with chloroform, gave  $\alpha + 4.17^\circ$ , whence 2 dm. tube, whence  $[\alpha]_D + 43.27^\circ$ .

1.0049, made up to 20 c.c. with ethyl alcohol, gave  $\alpha + 4.8^\circ$ , whence 2 dm. tube, whence  $[\alpha]_D + 48.26^\circ$ .

A mixture of approximately equal quantities of the two phthalates melted indefinitely at about  $5^\circ$ .

*1-sec-Octyl Alcohol*.—The active acid esters readily dissolve in aqueous potash, and are quickly hydrolysed, when the solution is boiled in alcohol. Being insoluble in alkaline solutions, is easily extracted with ether, and is then fractionated under reduced pressure. Several comparative experiments were carried out with the dextro-ester, and the results alone are recorded. The following are the rotations observed at three separate preparations: in I the acid ester was hydrolysed with the calculated amount of potash; in II it was partially hydrolysed with twice the calculated amount; in III the residue from II was hydrolysed completely with a large excess of potash:

I.	In a 50 mm. tube at $17^\circ$	gave $\alpha + 4.00^\circ$ .
II.	" 100 mm. " $17^\circ$ "	" $8.00^\circ$ .
III.	" 24.66 mm. " $20^\circ$ "	" $1.99^\circ$ .
I + II.	" 200 mm. " $20^\circ$ "	" $15.93^\circ$ .

Similar products to these were mixed and redistilled twice, and the pure *1-sec-octyl alcohol* boiled at  $86^\circ/20$  mm. The density at

$n_D^{20}$  0.8221 and  $D_4^{20}$  0.8229, this being slightly higher than recorded by Beil (*Annalen*, 1880, **203**, 28), who gave  $D_4^{20}$  0.8193 for the same alcohol.

The refractive index was found to be  $n_D^{20}$  1.424, whence the molecular refraction is 40.28, the calculated value being 40.44.

The rotation was observed in a 2-dm. tube at 17°, the mean of seven concordant readings being  $\alpha + 8.125^\circ$ , whence  $[\alpha]_D^{20} + 9.87^\circ$ . It was also observed in solution:

1.05, made up to 20 c.c. with chloroform, gave  $\alpha + 0.93^\circ$  in a 2-dm. tube, whence  $\alpha_D + 9.00^\circ$ .

1.03, made up to 20 c.c. with ethyl alcohol, gave  $\alpha + 1.07^\circ$  in a 2-dm. tube, whence  $[\alpha]_D + 9.79^\circ$ .

The pure dextro-alcohol was reconverted into the acid phthalate, and without recrystallisation had  $[\alpha]_D + 48.19^\circ$  in ethyl alcohol.

Our thanks are due to Mr. Tom Thoruley, who carried out preliminary work in the preparation of this and several other racemic phthalic esters, as also to the Research Fund Committee of the Society for a grant which has defrayed much of the cost of this investigation.

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## CCL.—*The Alkyl Compounds of Gold.*

By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

It is noteworthy that organo-metallic compounds can in many cases be conveniently prepared by the action of zinc ethyl on the halogen compounds of the metals was made by Buckton (*Proc. Roy. Soc.*, 1869, **9**, 309); he thus obtained mercury diethyl, lead tetraethyl, silver tetraethyl, but was unable to apply the same reaction to the preparation of alkyl compounds of silver, platinum, or copper. Stannard and Peachey showed (*Proc.*, 1903, **19**, 290) that the alkyl compounds are conveniently prepared by the action of the zinc ethyl reagent on stannic chloride or on halogen derivatives of tin and tin compounds; since that time, a series of papers on this reaction and its developments has appeared by Pfeiffer and his collaborators (*Ber.*, 1904, **39**, 319, 1125, 4617, &c.), but the authors have apparently overlooked the English work on the subject. From this and allied work, it has been learnt that alkyl



compounds, such as those of tin, silicon, mercury, &c., are readily prepared by the action of alkyl magnesium halogen derivatives on the halogen compounds of the elements. By means of the Grignard reagent, there have hitherto been prepared representatives of classes of alkyl compounds of those elements which belong to groups II to VII of the periodic classification. The existence of these was either demonstrated or foreseen by Frankland (*Journ. Chem. Soc.*, 1850, 2, 297).

Pope and Peachey have, however, recently prepared trimethylplatinic hydroxide and its salts by the aid of the Grignard reagent (*Proc.*, 1907, 23, 86), and in the present paper we describe the preparation of diethylauric bromide by the aid of magnesium ethyl bromide. We are thus now acquainted with organo-metallic compounds of elements of groups I to VIII of the periodic classification, and can consequently conclude that members of the eight vertical groups yield stable alkyl compounds. In the original periodic table, Mendeléeff places gold and platinum in horizontal series 10 (*Lausan*, 1871, *Supp. Bd.*, 8, 151); this is of interest in connexion with his conclusion that elements occurring in the higher even-numbered series do not yield stable alkyl compounds, and that if alkyl compounds were obtained from such elements they would be totally different in properties from previously known organo-metallic substances. Trimethylplatinic iodide and diethylauric bromide are salt-like substances of constitution according with the quadrivalency of platinum and trivalency of gold; they correspond roughly in properties to such substances as triethylstannic and diethylthallic salts, and it does not appear legitimate to conclude that Mendeléeff's prediction is verified by the discovery of the alkyl compounds of platinum and gold.

Evidence was obtained by Wanklyn and by Frankland (*Phil. Mag.*, 1859, 9, 341, 345) of the existence of potassium sodium ethyl,  $C_2H_5K$  and  $C_2H_5Na$ ; although neither was isolated, it appears from the experimental facts quoted by the authors that ethyl iodide acts on sodium ethyl with formation of sodium iodide and gaseous products. No indication was given of the production of a compound having the composition  $C_4H_{10}$ . In the case of the organo-gold compounds, behaviour of this kind has been observed; there seems to be no tendency to the production of the simpler substance,  $C_2H_5Au$ , but the complex compound,  $(C_2H_5)_3AuBr$ , has been prepared. These facts perhaps illustrate better than has been hitherto possible the recognised aspect of the periodic law. In a high group of the periodic table, group V, for example, whilst triethylphosphine

gally combines with ethyl iodide, triethylbismuthine does not; the tendency of the trivalent element to become quinquivalent diminishes as the atomic weight increases. In the low numbered group I, the converse is to be concluded from the facts that the compounds,  $C_2H_5Na$  and  $(C_2H_5)_2AuBr$ , are known, whilst the compounds,  $C_2H_5Au$  and  $(C_2H_5)_2NaI$ , have not yet been prepared.

### *Diethylauric Bromide, $(C_2H_5)_2AuBr$ .*

As the preparation of diethylauric bromide presents some experimental difficulties, it will be convenient to state precisely the conditions under which we have been able to obtain the substance. Magnesium (5 grams) is converted into magnesium ethyl bromide by treatment with the calculated quantity of ethyl bromide dissolved in anhydrous ether (200 c.c.), care being taken that no excess of magnesium is left in the solution. The solution of the original reagent is then run very slowly into a solution of dry auric bromide (22 grams) in ether (150 c.c.) by means of a dropping funnel; the latter solution is well cooled by a mixture of ice and salt, and constantly stirred during the process. Reaction is instantaneous, and during the admixture metallic gold begins to separate out; as soon as the whole of the Grignard reagent has been run in, powdered ice is cautiously added and the mixture then allowed to warm up to the room temperature; water and glacial acetic acid are then added, and the liquid extracted several times with light petroleum. The petroleum extract is washed several times with water and transferred to a large basin, which is then placed in a warm draught cupboard so that the petroleum is enabled to evaporate rapidly at a temperature of 25-30°. When evaporation is complete, an almost colourless, crystalline residue is left in the basin and this, after one crystallisation by spontaneous evaporation of its solution in light petroleum, yields pure diethylauric bromide. Under the most favourable circumstances, a yield of 2-3 grams of the pure substance is obtained from the quantities used above.

The auric bromide used in this method of preparation can be replaced by auric chloride without diminishing the yield, but no appreciable yield was obtained on mixing the auric bromide and magnesium ethyl bromide solutions at the temperature of boiling liquid air. The yield is diminished by running the auric bromide solution into that of the Grignard reagent. Attempts to prepare the substance by the action of zinc ethyl on auric chloride, both in ethereal solution, were unsuccessful; the two solutions react with great

violence, metallic gold is deposited, and no organic product is isolated.

*Diethylauric bromide* crystallises from light petroleum in colourless, doubly-refracting needles, which melt at  $58^{\circ}$  with decomposition and have an odour resembling that of monochloroauric bromide. It is very soluble in benzene, petroleum, chloroform, ether, much less so in alcohol, and insoluble in water. The substance volatilises readily at the ordinary temperature in air or in a vacuum, and would doubtless lend itself to vapour density determination; when heated to about  $70^{\circ}$ , it decomposes explosively, leaving a residue of the metal and giving volatile products which, from their odour, do not consist of simple hydrocarbons, like butane, or of halogen derivatives of the same.

The analysis of the compound is conveniently effected by dissolving the substance in chloroform, adding a chloroform solution of bromine, slowly evaporating to dryness, and weighing the residue which is obtained after ignition:

0.2082 gave 0.1216 Au. Au = 58.41.

$(C_2H_5)_2AuBr$  requires Au = 58.82 per cent.

Diethylauric bromide is extremely sensitive to reagents. It is precipitated as silver bromide with solutions of silver salts, and is once acted on by bromine, ammonia, or nitric acid. When exposed to light in contact with water, metallic gold is gradually deposited; reduction also takes place rapidly when its solutions are warmed, so that the crystallisation of diethylauric bromide from all but the most volatile solvents is difficult.

#### *Monoethylauric Dibromide, $(C_2H_5)_2AuBr_2$*

On adding a dilute solution of bromine in chloroform to a solution of an equimolecular proportion of diethylauric bromide in the same solvent and allowing the solution to remain at the ordinary temperature, crystals of monoethylauric dibromide are gradually deposited. After most of the chloroform has spontaneously evaporated, the crystalline deposit is separated and washed with chloroform.

*Monoethylauric dibromide* is sparingly soluble in the most volatile organic solvents, and is moderately soluble in warm water. It crystallises in transparent, dark ruby-red, doubly-refracting plates with square ends; on heating, it decomposes gradually before melting. It was analysed by decomposing a known weight with a chloroform solution of bromine and weighing the metal remainder after ignition:

0.122 gave 0.1682 Au. Au = 51.09.

$(C_2H_5)_2AuBr_2$  requires Au = 51.07 per cent.

This compound is much more stable than diethylauric bromide, as is shown from the fact that its solutions may be heated to a much higher temperature than those of the latter without the occurrence of reduction. It is immediately converted by ammonia into a bright yellow powder, which is insoluble in water or acetone; this product decomposes violently on gentle heating.

It is interesting to note that, whilst diethylauric bromide is quite colourless, monoethylauric dibromide possesses a red colour almost, though not quite, as deep as that of auric bromide.

#### *Aminodiethylauric Bromide, $(C_2H_5)_2AuBr, NH_3$ .*

On gently warming diethylauric bromide with dilute aqueous ammonia, solution rapidly occurs, and after evaporation in a vacuum desiccator a white, crystalline substance remains. The latter may be recrystallised from benzene, and forms transparent, non-refracting, colourless needles, which decompose gradually on heating at about 60°. It is soluble in benzene, acetone, chloroform, ammonia, or dilute hydrochloric acid; the solution in hydrochloric acid may be boiled without the occurrence of reduction, and the solution is not precipitated by platinic chloride, although on prolonged heating metallic gold is deposited. The aqueous acetone solution does not precipitate silver bromide with silver salts.

For analysis, a weighed quantity of the substance was treated with a 10 per cent form solution of bromine, as in the previous cases, and the residue ignited and weighed as metal. The reaction with the bromine solution is much more violent than in the other cases:

0.128 gave 0.0728 Au. Au = 55.66.

$(C_2H_5)_2AuBr, NH_3$  requires Au = 55.98 per cent.

This substance appears to be the first amino-compound of gold which has been described, and in type of composition does not correspond to any other amino-compounds which have been prepared. It might possibly be classed with the compound of ferric chloride and ammonia,  $FeCl_3, NH_3$ , described by H. Rose (*Ann. Phys. Chem.*, 1832, 34, 212).

The investigation of these substances and of the alkyl compounds of the other metals of groups I to VIII of the periodic classification is being continued; in view, however, of the poor character of the product obtained, the work necessarily proceeds but

We desire to express our thanks to Mr. George Matthey, F.R.S., for generously allowing us the use of the large amounts of goods which have been required in the work.

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### CCIII.—*Methyl Ethers of some Hydroxyanthraquinones*

By ARTHUR GEORGE PERKIN.

THE results of an examination of Chay root (*Oblendaulia umbellata*, an Indian dyestuff) made several years ago (Perkin and Hummel, *Trans.*, 1893, **64**, 1160, and 1895, **68**, 217) indicated that it contained, in addition to alizarin and its glucoside, ruberythrin, and numerous other non-tinctorial substances. The most interesting of the latter consisted of dimethyl ethers of anthragallol, the *o*-methyl ether of alizarin, the monomethyl ether of hystazarin, and *m*-hydroxyanthraquinone, and these compounds were present in the sample of root examined, partly in the form of glucosides and partly in the free state.

Somewhat recently Böck (*Monatsh.*, 1902, **23**, 1008) studied the methylation of anthragallol and obtained a dimethyl ether of a colouring matter, which did not agree in melting point with any of the anthragallol dimethyl ethers found to be present in Chay root. As the result of this single observation, Böck makes the following statement: "Es erscheint mir demnach nicht ausgeschlossen, dass die Äthere Perkin's und Hummel's nicht die vermutete Verbindung zukommt, dass sie vielleicht hydrierte Derivate sind. . . . Ich glaube ich dass eine wirkliche Trennung des Methyläthers des Anthragallols, Alizarins und anderer Oxyanthrachinone wie sie in der Wurzel von *Oblendaulia umbellata* vorkommen, keineswegs so leicht sein wird wie es nach den Arbeiten Perkin's und Hummel's den Anschein hat."

The statements of Böck were noted at the time, but no steps were taken to reply to these criticisms, for although it was quite possible that an error had arisen in regard to one of the three anthragallol dimethyl ethers described as existing in Chay root, it appeared impossible, on considering the facts given in the paper, that the compounds in question could be otherwise than derivatives of anthraquinone. To attempt a re-examination of the root itself would have been hardly worth while, and the subject would have remained

and had not some residues remaining from the former work been discovered. The separation of the various substances was effected according to the methods given in the previous work, and will be here alluded to in the order in which they occur in that part of the paper.

*Anthragallol Dimethyl Ether (A)*, m. p. 209°.—This compound, as already shown, is distinguished by the fact that its ammonium salt is readily isolated in the crystalline condition, and serves to distinguish it from the anthragallol dimethyl ether (*B*) which under the conditions employed is not precipitated in this manner. A re-examination of the substance corroborated previous statements, and the melting point, 209°, remained unaltered, although numerous attempts at further purification were resorted to. Owing to the fact that the colour of its alkaline solutions disappears on treatment with zinc dust, it returns on exposure to air, it seemed obvious that, taken in connection with the evidence previously given, this compound is a derivative of anthraquinone. On the other hand, should it contain a phenolic or allied grouping by gentle oxidation with chromic acid the corresponding hydroxyanthraquinone dimethyl ether would be formed, and such a method was employed for the determination of the constitution of members of this class which are present in the roots of the *Ventilago madraspatana* (Trans., 1894, 66, 923). It was found, however, that when the anthragallol dimethyl ether (*A*) was subjected to the action of chromic acid in acetic acid solution, an oxidation of this character did not occur, and it suffered gradual destruction with the formation of phthalic acid as previously noted.

The *anthragallol trimethyl ether* (*B*) was prepared with some difficulty from anthragallol dimethyl ether of this colouring matter, although from his analytical figures he was unable to pronounce this to be a pure compound. As is well known, the difficulty in dealing with phenolic compounds of this class is to methylate the hydroxyl group in the ortho-position relatively to the carbinol group, and this, frequently impossible without the introduction of methyl sulphate, was a fairly sure indication of the presence of such a grouping. In attempting to methylate one of the natural anthragallol dimethyl ethers, this difficulty was not necessarily avoided, as both compounds might already possess a methoxy group in the ortho-position. To determine this point as regards the anthragallol dimethyl ether (*A*), it was dissolved in methyl-alcohol, the solution gently warmed, and treated with equivalent quantities of methyl-alcoholic potash and methyl sulphate. A deep red coloration was given by the final addition of the former. The mixture treated with boiling water gave a crystalline, pale yellow substance which was collected and washed with hot dilute alkali, and then melted at 168°. It was practically pure, for after two

recrystallisations from alcohol and acetic acid this melting point remained unaltered:

Found, C = 68.77; H = 4.78; CH<sub>3</sub> = 14.83.

C<sub>14</sub>H<sub>11</sub>O<sub>5</sub>(CH<sub>3</sub>)<sub>3</sub> requires C = 68.46; H = 4.70; CH<sub>3</sub> = 15.10 per cent.

It consisted of pale yellow needles sparingly soluble in alcohol, was evidently *anthragallol trimethyl ether*. The melting point agreed with that given by Bock for his ether, but there was every indication in this case that a pure compound had been obtained. Methylation proceeds so easily that from only a very small quantity of the starting ether sufficient of the fully methylated product could be isolated for purposes of characterisation, and accordingly it appears evident that in the original substance there is present a methoxy-group in the ortho-position relatively to the carbinol group.

As previously stated, the anthragallol dimethyl ether did not form a crystalline ammonium salt when its hot alcoholic solution was treated with ammonia, and it appeared interesting to observe if, by means of alcoholic potassium acetate (Trans., 1899, **76**, 433), a corresponding potassium compound would be precipitated. Such was found to be the case, a crystalline precipitate separating almost immediately.

Found, K = 11.73.

C<sub>16</sub>H<sub>11</sub>O<sub>5</sub>K requires K = 12.10 per cent.

It consisted of glistening, violet leaflets, which on exposure to air of the laboratory suffered somewhat rapid decomposition with evolution of the free dimethyl ether. This proneness to evolve carbon dioxide is not exhibited by the potassium salts of anthraquinizarin, and allied colouring matters. The compound is soluble in water with a crimson colour, and the solution is unaffected on being raised to the boiling point, at least for short periods.

*Anthragallol dimethyl ether (B)* in general properties closely resembles the substance (A), but is characterised by the fact that its ammonium salt is readily soluble in alcohol. An elaborate series of purifications indicated that the melting point previously given for this compound (225–227°) is slightly too low and should be 228–230°, and the acetyl derivative melts at 176–178° instead of 175°. When treated with chromic acid in acetic acid solution it gave no indication of a reduced anthraquinone nucleus, and, when methylated, was readily transformed into anthragallol trimethyl ether, m. p. 168°. It must therefore, the constitution originally assigned to it. Potassium acetate did not precipitate a potassium salt from a hot alcoholic solution of this compound, a property which again distinguished it from the anthragallol dimethyl ether (A).

*Alizarin α-Methyl Ether*.—This interesting compound has not previously been produced synthetically from alizarin, all attempts to date

having resulted in the formation of the corresponding methoxy-derivative. The methoxy-group present in this substance is more readily hydrolysed than is usually the case, for prolonged digestion with boiling baryta water is sufficient for this purpose, the precipitate consisting of barium alizarate thus separating. This property therefore accounts for the difficulty in obtaining either this compound or alizarin dimethyl ether by means of methyl iodide, for this process a prolonged digestion in the presence of free alkali is necessary. A re-examination of the substance confirmed the melting point  $178^{\circ}$ — $179^{\circ}$ , previously given and it was found that by means of potassium potash a sparingly soluble potassium salt can readily be prepared. This compound, which crystallises in garnet coloured, prismatic needles, has evidently the formula  $C_{15}H_6O_4K$ , but as it was necessary to reserve the small quantity of the alizarin methyl ether available for more important experiments, it was not further studied. To be certain that the methyl ether contained but one free hydroxyl group, it was acetylated, and the acetyl derivative, which melted at  $212^{\circ}$ , was analysed by Zeisel's method:

Found  $CH_3 = 5.05$ .

$C_{15}H_6O_4 \cdot C_2H_5O$  requires  $CH_3 = 5.06$  per cent.

It was therefore a monoacetyl compound.

As a further proof of the constitution of the methyl ether, it was necessary to study its behaviour on methylation, for containing, as is noted, the ortho-methoxy-group, the production from it of alizarin dimethyl ether should proceed without difficulty. Employing methyl iodide such was found to be the case, and on treating the product of the reaction with hot water, pale yellow, glistening needles formed. These consisted of the substance in a practically pure condition, but were recrystallised from a mixture of acetic acid and alcohol:

Found  $CH_3 = 11.21$ .

$C_{15}H_6O_2(O \cdot CH_3)_2$  requires  $CH_3 = 11.19$  per cent.

The substance melted at  $210^{\circ}$ — $211^{\circ}$ . Alizarin dimethyl ether has been prepared by Graebe (*Ber.*, 1905, **38**, 152), by the oxidation of alizarin dimethyl ether,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{O}) \\ \text{C}(\text{H}_2) \end{smallmatrix} > C_6H_2(O \cdot CH_3)_2$ , and also by Graebe and Thode (*Annalen*, 1906, **349**, 207), by the direct methylation of alizarin with methyl sulphate. As the melting point of these authors to their compound is  $215^{\circ}$ , a small quantity of alizarin dimethyl ether was prepared according to the latter method, and it was found to be certain that the alizarin employed was pure, advantage being taken of a sample which in the course of the earlier work had been prepared from Chay root.

As when a considerable quantity of methyl sulphate was employed the melting point was



the main product of the reaction was alizarin *m*-monomethyl ether and only a trace of the dimethyl ether was obtained. The compound isolated by Graebe and Thode's method, was purified by crystallization from alcohol and acetic acid; it melted at 210—211°, and was identical with the product formed by the methylation of the alizarin monomethyl ether.

*Hystazarin monomethyl ether*, contained in Chay root, was examined, and as a result the melting point, 232°, and other properties assigned to this compound were corroborated. It was methylated by methyl sulphate in the manner previously described, and the crystalline product was washed with dilute alcohol and recrystallised from alcohol and acetic acid:

Found C = 71.61; H = 4.74; CH<sub>3</sub> = 11.13.

C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>·(O·CH<sub>3</sub>)<sub>2</sub> requires C = 71.64; H = 4.48; CH<sub>3</sub> = 11.19 per cent.

It consisted of pale yellow, glistening needles, melting at 235°, sparingly soluble in alcohol, and was evidently *hystazarin monomethyl ether*. As this compound did not appear to have been previously prepared, hystazarin, obtained by the method of Liebermann and Holtenmeyer (*Ber.*, 1902, 35, 1778), was methylated by means of dimethyl sulphate. The reaction proceeded without difficulty, and the product, which melted at 235—236°, was identical with that obtained from the natural monomethyl ether.

The *m*-hydroxyanthraquinone isolated from Chay root was evidently identical with the artificial compound as to nature, examination unnecessary. It was, however, methylated by means of methyl sulphate, and the product of the reaction crystallised from alcohol and acetic acid:

Found CH<sub>3</sub> = 6.18.

C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>·O·CH<sub>3</sub> requires CH<sub>3</sub> = 6.30 per cent.

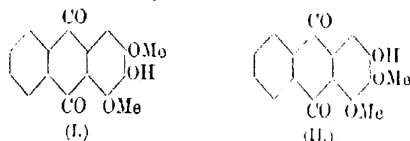
This *m*-hydroxyanthraquinone monomethyl ether formed pale yellow needles melting at 192—193°, and was found to be identical with the substance prepared in the same way from synthetical *m*-hydroxyanthraquinone.

• The so-called anthragallol dimethyl ether (*C*), previously described as existing in Chay root, could not, unfortunately, be reisolated. The amount previously isolated was very small, approximately 1 lb. from 2 cwt. of the root being all that was obtained. If it is synthetical anthragallol dimethyl ether (*loc. cit.*), m. p. 150—151°, a pure substance, then the compound (*C*) for which the melting point 212—213° was given cannot have been a distinct product, but must have been a mixture of the two anthragallol dimethyl ethers described (*B*), previously described. In any case this reasoning must be adopted by default, as the matter is not worthy of the method

trouble which a re-examination of the point would necessitate, and it accordingly can now only be considered as proved that Chay root contains two dimethyl ethers of anthragallol.

*Positions of the Methoxy-groups in the Anthragallol Dimethyl Ethers (A) and (B).*

Considering the difficulty with which the  $\alpha$ -hydroxyl group present in alizarin and the allied hydroxyanthraquinones is methylated, and, taking into consideration the comparative ease with which the two anthragallol dimethyl ethers of Chay root are converted into anthragallol trimethyl ether, it appeared extremely probable that both compounds contain a methoxy-group in the  $\alpha$ -position and would possess one or other of the following formulae:



Further, it is reasonable to suppose that Bick's synthetical ether would have the third possible formula and contain a free hydroxyl in the  $\alpha$ -position, on account of the difficulty with which the latter group is methylated.

As previously shown, the methoxy-group present in alizarin dimethyl ether somewhat readily suffers hydrolysis in boiling alkaline solutions, and it seemed therefore likely that the corresponding group present in the two anthragallol dimethyl ethers would be hydrolysed at least more readily than those present in the meta-positions relative to one or other of the carbonyl groups. Should this be the case, anthragallol monomethyl ethers possessing respectively the combinations  $(\text{OH} : \text{OH} : \text{OMe} = 1 : 2 : 3)$  and  $(\text{OH} : \text{OMe} : \text{OH} = 1 : 2 : 3)$  would be produced, and the identity of each could be ascertained. Thus the former grouping is that of a methoxyalizarin, a compound which would be soluble in alkali with a blue tint, whereas the latter, which represents a methoxypurpuroxanthin, should yield red alkali salts.

To investigate this point a small quantity of the anthragallol dimethyl ether (A) was dissolved in 10 per cent. potassium hydroxide solution, and the liquid heated to  $160^\circ$  in a sealed tube for five hours. The product when cold appeared as a deep blue semi-solid, crystalline mass, which, on solution in boiling water and treatment with acid, deposited an orange-red precipitate. This was collected, well-drained, dissolved in boiling alcohol, and cautiously precipitated with hot water, when it separated completely on cooling in a crystalline form.

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Found  $\text{CH}_3 = 5.18$ .

$\text{C}_{14}\text{H}_9\text{O}_2(\text{O}\cdot\text{CH}_3)_2$  requires  $\text{CH}_3 = 10.56$  per cent.

From the analysis it is evident that this product, which gave coloured needles melting about  $195^\circ$ , was a mixture of a monomethyl ether and a dimethyl ether of anthragallol. On the other hand, the former gave the necessary information, for, as the substance was a monomethyl ether, it dealt with a blue colour, and readily dyed mordanted cloth. There could be little doubt that the monomethyl ether present consisted of *methoxyalizarin*.

An experiment carried out with the anthragallol dimethyl ether under the same conditions, at  $160^\circ$ , showed that at this temperature practically no hydrolysis of a methoxy-group occurs, for the melting point of the recovered substance was  $225^\circ$ , and its general properties were identical with those of the original compound. Employing, however, a temperature of  $180^\circ$  for five hours, it was evident that some change had now occurred, for, although the alkaline solution was still red and no trace of blue could be detected, on acidification a red precipitate separated. After being crystallised by the addition of boiling water to its hot alcoholic solution it commenced to sinte at  $180^\circ$  and melted completely at  $212-213^\circ$ .

Found  $\text{CH}_3 = 8.10$ .

$\text{C}_{14}\text{H}_9\text{O}_2(\text{O}\cdot\text{CH}_3)_2$  requires  $\text{CH}_3 = 10.56$  per cent.

This product was evidently a mixture, but the fact that its alkaline solution possessed a red colour indicated that the monomethyl ether which had been formed was *methoxypurpurazanthin* ( $\text{OH}:\text{OMe}:\text{OH}$ , 1:2:3). The corresponding ethoxy-derivative has been previously shown (Trans., 1899, 76, 446) to be produced when mono-*o*-methoxyanthragallol is heated with ethyl iodide at  $230^\circ$ , and the solutions of the alkali salts of this compound are red. These results therefore adduce considerable proof that the formulæ I and II given above represent respectively the anthragallol dimethyl ethers (Ia and Ib), but in case, although this was hardly likely, some change other than hydrolysis of the methoxy group had been caused by the alkaline temperature employed, the hydrolysis of these compounds by means of sulphuric acid was now studied.

Experiments first carried out with alizarin *o*-methyl ether, and then with alizarin dimethyl ether in presence of the concentrated acid at  $160^\circ$ , clearly showed that the *o*-methoxy-group is the most readily attacked in this manner. Thus whereas during half-an-hour's digestion the former compound gives alizarin, the latter, although somewhat more readily, gives alizarin *m*-methyl ether, which, after purification

melting at 224—226.\* Finally, anthragallol trimethyl ether, when heated in this respect, gave at first a compound soluble in alkali with a red coloration, due no doubt to the formation of the dimethyl ether (OH:OMe:OMe = 1:2:3), but on longer heating further hydrolysis occurred with formation of a monomethyl ether soluble in alkalis with a blue colour, and possessing mordant-dyeing properties. The latter compound, which for reasons given above is evidently the monomethyl ether (OH:OH:OMe = 1:2:3), on prolonged heating with concentrated sulphuric acid at 100°, did not appear to suffer further change, a point of interest in connexion with the constitution of the anthragallol dimethyl ether (B).

*Action of Sulphuric Acid on the Dimethyl Ether (A).—*On heating this compound with excess of the acid to 100°, the alkaline solution of the product examined from time to time soon exhibited a violet tint and finally became blue. It was isolated by addition of water to the hot solution, was purified by crystallisation from alcohol and consisted of orange-red needles melting at 231—232°. Evidently this substance, which readily dyed mordanted calico, is the same compound, in a purer condition, as that formed by the action of potassium hydroxide solution on this anthragallol dimethyl ether, and also by digesting anthragallol trimethyl ether with sulphuric acid; and there can be no doubt that it possesses the constitution of a methoxylizarin. It is referred in one of the former communications (*loc. cit.*) that when this substance is heated with hydrochloric acid at 150° for an hour, a product of this nature, but evidently contaminated with anthragallol, is formed, and Böck (*loc. cit.*), by the action of sulphuric acid on his dimethyl ether, obtained this anthragallol monomethyl ether, m. p. 233—235°, apparently in a pure condition. As shown above, this methoxylizarin is but slowly, if at all, attacked by continued heating with sulphuric acid at 100°.

*Action of Sulphuric Acid on the Dimethyl Ether (B).—*By the action of the acid on this substance at 100° for half an hour, the product on addition in alkali gave a red coloration which differed but little from that given by the original compound. Even after two hours no perceptible change occurred in this respect. The precipitate formed by the addition of water exhibited a more orange tint, and probably consisted, at least in part, of an anthragallol monomethyl ether, but on continuing the digestion for seven hours the compound thus produced was now soluble in dilute alkali with a green coloration

\* This has been previously observed. Trans., 1899, **76**, 416; that this melting point agrees with that given by Schmeck and Marchalski (*loc. cit.*), namely, 224—226°, but as it has now been prepared by the author in the three distinct ways mentioned, it is necessary to assume that the lower figure is correct.

and after purification consisted of orange-red needles, which readily melted under pressure. The acetyl derivative of this colouring matter was obtained in pale yellow needles melting at  $182-183^{\circ}$ , and was well characterised by its melting point and by its being identical with acetylanthragalol.

This result, therefore, considered in conjunction with the previous experiment, shows clearly that in this compound no methoxy-group can be present in the position 3, for it has been found that in anthragallol monomethyl ether,  $\text{OH}:\text{OH}:\text{OMe}=1:2:3$ , is fairly stable towards sulphuric acid at  $100^{\circ}$ , and, moreover, its formation at any stage of the reaction would have been indicated by the deepening colour of its alkali salts.

Accordingly, therefore, whereas the methoxy-groups in anthragallol dimethyl ether (A), m. p.  $209^{\circ}$ , occupy the positions 1 and 3 (formula I), in the anthragallol dimethyl ether (B), m. p.  $230-232^{\circ}$ , they occupy the positions 1 and 2 (formula II). It is interesting to observe that the formation of sparingly soluble potassium salts effected by anthracene methyl ether, and by anthragallol dimethyl ether, when alcoholic potassium acetate is employed, is in harmony with the previous work in connexion with anthraquinone colouring matters, from which proof was deduced that the reactive hydroxyl occupies the meta position relative to the carbonyl group.

As regards Böck's criticism (*loc. cit.*), that he believes that the methyl ethers of anthragallol, &c., present in Chay root, cannot be separated by any means so easily as the work of Perkin and Hummel indicates, comment is almost unnecessary. In the first place, the author does not produce the faintest evidence that he has effected an examination of Chay root, or even that he has been in possession of this natural dyestuff; again, there is no assertion in the paper of Perkin and Hummel that the separation of the mixed substance is easy or of a simple character. Thus it is stated on page 825 (*loc. cit.*) "The methods employed for the separation of the yellow substance in Chay root, soluble in baryta water, being *somewhat intricate*, the tables on page 825 are appended with a view to explain the method pursued more clearly." Possibly it is in connexion with the latter that Böck's criticism has arisen; if so, it should be said that it is obviously unnecessary at the time to remark that these tables did not represent a scheme of quantitative analysis, for such an idea could not occur to anyone who had read these papers carefully.

*Note on the Emodin Methyl Ether contained in the Ventriculus of Madraspatana.*

It has been recently shown by O. A. Oesterle (*Arch. Pharm.*, 1907, 245, 287) that the wood of *Morinda citrifolia* contains a natural

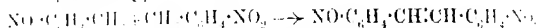
of a trihydroxymethylantraquinone melting at  $216^{\circ}$ , and this substance he considers is very probably identical with the compound of similar constitution, melting at  $200^{\circ}$ , isolated by Perkin and Hummel from the root bark of *Ventilago madraspatana* (Trans., 1894, 66, 223). Although it is quite possible in dealing with substances of this nature, and which exist in plants in conjunction with other compounds possessing closely similar properties, that an error of a degree or two in their melting point might occasionally arise, it seemed unlikely in this case that the conjecture of Oesterle was correct. The substance of Perkin and Hummel, which was proved without doubt to be a monomethyl ether of emodin, was produced by the action of two distinct isomeric compounds,  $C_{16}H_{14}O_4$ , probably emodin derivatives, with chromic acid, and was also isolated in small quantity from the root bark of *Polygonum cuspidatum* (Trans., 1895, 68, 1084). As the author was in possession of a small quantity of this emodin methyl ether, it was crystallised from acetic acid and benzene, and was found to melt at  $200-201^{\circ}$  (the melting point previously given is  $200^{\circ}$ ). The acetyl derivative, crystallised from alcohol and acetic acid, melted as before at  $185-186^{\circ}$ , and when this was hydrolysed with alcoholic potash, the regenerated methyl ether melted at  $201^{\circ}$ . This emodin methyl ether, from *Ventilago madraspatana*, was, therefore, evidently pure, and the surmise of Oesterle is accordingly incorrect. There is no evidence that this author has examined *Ventilago madraspatana*, and it is to be deprecated that criticisms of this kind should be submitted to publication without fuller proof. Even when it is not always possible to retain specimens of such rare substances, as it had not this been the case in the present instance, considerable trouble would have been occasioned in the preparation of sufficient substance from the root, in order that the minor points discussed above could be answered.

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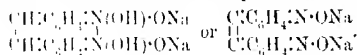
CCIV. *The Colouring Matters of the Stilbene Group.*  
 Part IV. *The Action of Caustic Alkalis on*  
*p*-nitrotoluene and its Derivatives.

By ALBERT GEORGE GREEN, ARTHUR HUGH DAVIES, and RICHARD  
 SMITH HORSFALL.

As the results of investigations conducted by Green in conjunction with former collaborators (*Ber.*, 1897, **30**, 3097; 1898, **31**, 197; *Trans.*, 1904, **85**, 1124, 1432), the view was advanced that the deep coloured (red, violet, or blue), unstable intermediate products which mark the first stage of the action of caustic alkalis on *p*-nitrotoluenes and its derivatives are to be regarded as nitrosostilbenes, formed according to the typical scheme:



This conclusion was arrived at from a study of the products of oxidation, the compounds themselves being too unstable to admit of isolation. The deep colour of the alkaline solutions of these compounds (when neutral they are pale yellow) was accounted for by assuming for the alkali salts a tautomeric quinonoid form, such as:



The reaction appears to be common to *p*-nitrotoluene and its derivatives, but is greatly facilitated by the presence of other negative groups in the ortho-position with respect to the nitro group. This is seen, for example, in the more ready condensation of *p*-nitrotoluenesulphonic acid compared with that of *p*-nitrotoluene itself. At the same time, it is noteworthy that in those cases in which the reaction is greatly accelerated by the presence of a strongly electronegative group, such as  $\text{SO}_3\cdot\text{C}_6\text{H}_4$ , CN or NO<sub>2</sub>, the colour of the intermediate compound is blue instead of red.

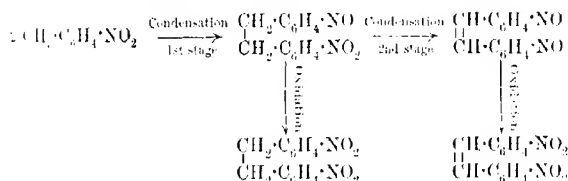
In order to investigate the effect of different ortho-substituents and to obtain further light on the course of the reaction, we have examined the behaviour to caustic alkalis of *p*-nitrotoluenesulphonates of its *o*-methyl-, *o*-methoxy-, *o*-cyano-, and *o*-carboxy-derivatives. As in the cases previously investigated, we have endeavoured to

This fact was first recognised by Green and Stainton. The latter observed close parallelism between the influence of various ortho-substituents on the rate of the hydrazination of the methyl group when derivatives of *p*-nitrotoluenesulphonates were submitted to the stilbene condensation, on the one hand, and to Stainton's condensation with nitrosodimethylaniline, on the other.

characterise the intermediate compounds by oxidation to the stable stilbene compounds by means of air or hypochlorites.

In the cases examined by Green, Marsden, and Scholefield (*o*-chloro-derivative and the *o*-phenylsulphonate), only stilbene compounds were obtained on oxidation, and no formation of a dinitrodibenzyl compound was observed, although Green and Wahl had previously obtained from *p*-nitrotoluenesulphonic acid both dinitrodibenzylsulphonic acid and dinitrostilbenedisulphonic acid, according to the conditions under which the alkaline condensation was performed. We have now found that the ultimate product of oxidation largely depends on the reactivity of the particular derivative. Thus, whilst the *o*-cyano-derivative gave only the corresponding stilbene compound, we obtained from the methyl, methoxyl, and ethoxyl derivatives the corresponding dibenzyl compounds; and from *p*-nitrotoluene itself, like its sulphonic acid, either dinitrodibenzyl or dinitrostilbene, according to the conditions employed. It is worthy of note that the derivatives which yield by preference dibenzyl compounds are those which react least easily and give red condensation products, whilst the derivatives which yield chiefly stilbene compounds are those which react most readily and form violet or blue condensation products.

The results point to the conclusion that the alkaline condensation occurs in two stages, which may be more or less concurrent according to the degree of reactivity of the substance. The product of the first stage gives rise on oxidation to a dinitrodibenzyl, that of the second stage to a dinitrostilbene. This is shown by the following scheme:



When oxidation accompanies condensation, as in the experiments recorded, it would only depend on the speed with which stage one passes into stage two whether the first or the second condensation product was that chiefly attacked by the oxygen. Substituents which increase the reactivity of the substance would therefore favour the formation of stilbene compounds. That this is in fact the case will be evident from the following table.



*Relative Influence of Various ortho-Substituents on the Reactivity of the Methyl Group in para-Nitrotoluene Derivatives.*

We have endeavoured to obtain an approximate measure of the relative influence exerted by different ortho-substituting groups on the reactivity of the *p*-nitrotoluene complex by observing the minimum temperatures at which the colour formation commences under various conditions of alkalinity and molecular concentration. The experiments were performed as follows: 0.1 gram of *p*-nitrotoluene or the corresponding molecular quantity of one of its derivatives was dissolved in 1 c.c. of pyridine and 5 c.c. of pure methyl alcohol. The mixture was contained in a test-tube which could be warmed or cooled as required. Five c.c. of a saturated solution of potassium hydroxide in methyl alcohol (33 per cent. KOH) were added, the mixture was well stirred with a thermometer, and the minimum temperature was noted at which colour formation set in. The following results were obtained:

Substance.	Ortho-substituent.	Coloration produced.	Min. temp. of color.
<i>p</i> -Nitrotoluene .....	H	Crimson	7°
<i>p</i> -Nitro- <i>o</i> -xylene .....	CH <sub>3</sub>	"	70°
<i>p</i> -Nitro- <i>o</i> -tolylmethyl ether ..	OCH <sub>3</sub>	"	70°-72°
<i>p</i> -Nitro- <i>o</i> -toluidine .....	NH <sub>2</sub>	"	8°
<i>p</i> -Nitro- <i>o</i> -toluic acid .....	CO <sub>2</sub> H	"	7°-8°
<i>o</i> -Chloro- <i>p</i> -nitrotoluene .....	Cl	Violet	2°-3°
Phenyl- <i>p</i> -nitrotoluene- <i>o</i> -sulphonic acid .....	SO <sub>3</sub> CH <sub>3</sub>	Blue	50°-52°
<i>p</i> -Nitro- <i>o</i> -cyanotoluene .....	CN	"	10°-12°
2:4-Dinitrotoluene .....	NO <sub>2</sub>	"	10°

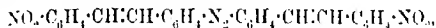
The reaction temperatures have, of course, only a relative significance, as they vary greatly with the concentration of reagents employed.

The comparison shows that, whilst the methyl, methoxymethyl, and carboxy groups have but little influence on the reactivity of the compound, the more strongly electronegative groups, sulphonic, cyano- and nitro-, exert a powerful effect, that of the nitro group being the greatest. This result is very analogous to the effect on the activity of the chlorine atom in chlorobenzene derivatives exerted by electronegative groups, such as the nitro- and sulphonic acid groups when occupying an ortho-position.

*Action of Caustic Alkalies and Air Oxidation on para-Nitrotoluene.*

By acting on *p*-nitrotoluene with alcoholic sodium hydroxide O. Fischer and Hepp (*Ber.*, 1893, **26**, 2231) obtained small quantities of dinitrotolubenzyl and dinitrostilbene. The main product of the

ation was, however, a sparingly soluble, orange-yellow substance, with the above authors term "dinitrostilbene," but which is really the dinitroazodistilbene,



by further condensation of the true dinitrostilbene which is explained. In order to prevent the formation of this condensation product, it is necessary to proceed in such a manner that the intermediate nitroso-compounds are oxidised as soon as they are formed. If, for instance, powdered *p*-nitrotoluene is covered with 33 per cent. methylalcoholic potash and slightly warmed, the formation of the red nitroso-compound commences at once. The conditions preclude the formation of hypochlorites, but the oxidation of the intermediate compound is readily effected by means of air. To obtain good results it is very necessary to take care that the oxidation keeps pace with the ester formation, since the nitroso-compound, if not at once oxidised, quickly undergoes further condensation. Five grams of *p*-nitrotoluene were placed in a wide-necked, conical flask together with 100 c.c. of cold 33 per cent. methylalcoholic potash. The red coloration which forms immediately disappears again on vigorous shaking giving place to a pale yellow, granular precipitate. The operation was continued in the cold with constant shaking until the color formation only took place slowly and the mixture had become a pale yellow, crystalline magma. This was then filtered by the aid of a pump, the precipitate washed with hot water and hot alcohol, and dried. The product recrystallised from benzene, formed pale yellow needles melting at 180–182°. It was evidently the known *1:4'-dinitrostilbenzyl*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ;

Calc. N = 10.56, 10.52.

$\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2$  requires N = 10.29 per cent.

Under the conditions employed above (reaction in the cold), dinitrostilbenzyl appears to be almost the sole product. If, however, the temperature of the mixture is slowly raised and the operation continued for a longer period, until finally the colour formation has completely ceased, the product is of a deeper yellow than before and consists chiefly of a compound which, after alternate crystallisation from nitrobenzene and from glacial acetic acid, was obtained in pale yellow leaflets or flat needles, melting at 292–294°. It proved to be *1:4'-dinitrostilbene*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , and probably represents this substance in a somewhat purer state than the one previously obtained. Fischer and Hepp assign to dinitrostilbene the melting point 272°, whilst Walden and Kernbaum (*Ber.*, 1890, 23, 137) give 280–285° as the melting point of their higher melting

isomeride. We have obtained no evidence of the formation of a second isomeride. Analysis gave the following results:

Found, C = 61.95; H = 3.57; N = 10.65, 10.55.

$C_{14}H_9O_4N_2$  requires C = 62.2; H = 3.7; N = 10.37 per cent.

The yield of the crude product is nearly theoretical.

In order to distinguish with certainty between stilbene and other derivatives in the above and other cases described in this paper, we have made use of the following test, which depends on the ready oxidation of the ethylene group. A small quantity of the substance is dissolved in a little pyridine, and to the cold solution is added one or three drops of an acetone solution of calcium permanganate. With stilbene compounds, the solution is at once decolorised, while with dibenzyl compounds the pink colour persists for several minutes, and if gently warmed.

#### *Action of Caustic Alkalis and Air on p-Nitro-oxytoluene*

The operation was carried out in the cold in the same manner as described above. In this case, also, the crude yield was almost theoretical. The product, after recrystallisation from glacial acetic acid, consisted of lemon-yellow needles, melting at 222–224°. It is not oxidised by potassium permanganate under the conditions described above, and is without doubt 4:4'-dinitro-2:2'-dimethyldibenzyl (4:4'-dinitro-*di-o-tolyl*),  $NO_2 \cdot C_6H_4 \cdot Me \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot Me \cdot NO_2$ .

The substance is somewhat sparingly soluble in most solvents and gave the following results on analysis:

Found, C = 64.14; H = 5.55; N = 9.58, 9.54.

$C_{16}H_{14}O_4N_2$  requires C = 64.0; H = 5.33; N = 9.33 per cent.

Under the conditions of the experiment, the corresponding stilbene derivative was not obtained.\*

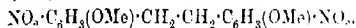
#### *Action of Caustic Alkalis and Air on p-Nitro-o-tolyl Methyl Ether*

The *p*-nitro-*o*-tolyl methyl ether employed was obtained by nitration of nitro-*o* cresol prepared by decomposition of the diazo compound of *p*-nitro-*o*-toluidine and purification in the manner described by Witt, Noelling, and Grandmougin (*Ber.*, 1890, 23, 3606). After recrystallisation from alcohol, the ether melted at about 72°.

The condensation and oxidation were effected in the same manner as before. The yield of the crude product, insoluble in alcohol, was nearly theoretical, namely, 4.9 grams from 5 grams of *p*-nitro-*o*-tolyl taken. The substance was crystallised two or three times from alcohol.

\* The dinitrodimethylstilbene and dinitrodimethoxystilbene have not yet been obtained and are at present undergoing investigation.

crystals, and then formed lemon-yellow leaflets melting at  $178-180^{\circ}$ . It proved to be 4:4'-dinitro-2:2'-dimethoxybiphenyl (4:4'-dinitro-2:2'-methylenebiphenyl),



Analysis gave the following results:

Found, C = 58.43; H = 4.80; N = 8.72.

$\text{C}_{15}\text{H}_{10}\text{O}_6\text{N}_2$  requires C = 57.83; H = 4.81; N = 8.43 per cent.

A methoxyl determination by Zeisel's method gave:

Found  $\text{CH}_3$  = 8.78.

$\text{C}_{15}\text{H}_{10}\text{O}_6\text{N}_2$  requires  $\text{CH}_3$  = 9.03 per cent.

The substance is not oxidised by permanganate under the conditions specified above.

Under the conditions employed, there was no formation of the corresponding stilbene derivative.\*

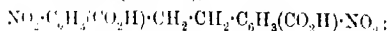
#### *Reaction of Caustic Alkalies and Hypochlorites on p-Nitro-o-toluic Acid.*

The p-nitro-o-toluic acid employed was obtained by saponification of p-nitrotol (see later) by boiling it for two or three hours with caustic acid diluted with half its volume of water. After recrystallisation from dilute alcohol, it formed long, colourless needles which melted about  $178^{\circ}$ . When heated with aqueous sodium hydroxide, it gave a deep violet-red coloration, which is converted into a yellow dye-stuff on longer heating. This colouring matter dyes coloured cotton direct in bright yellow shades, and is similar to Yellow 12. The behaviour of the carboxylic acid is therefore analogous to that of the corresponding sulphonic acid.

In order to oxidise the violet-red intermediate compound, we have worked in a similar manner to that employed for the sulphonic acid (see p. 198 and Wahl). Five grams of p-nitrotoluic acid were dissolved in 100 c.c. of water by means of 1.4 grams of sodium carbonate. To this solution were added 35 c.c. of sodium hypochlorite solution (7.4 per cent. active chlorine), followed immediately by 50 c.c. of sodium hydroxide (33 per cent. NaOH). The mixture was then rapidly heated to the boiling point, when the reaction sets in vigorously and the mixture boils spontaneously for about half a minute. Directly the mixture thickens and the mixture becomes pasty, but before any colour appears, and whilst there is still a small excess of hypochlorite left (that is, in about one minute from the commencement of the reaction), the whole contents of the flask must be poured into an excess of dilute hydrochloric acid (100 c.c. of concentrated hydrochloric acid and 300 c.c. of water) contained in a large beaker. The operation is somewhat difficult to carry out, as, if the

\* *Ibid.*

reaction is allowed to proceed a few seconds too long until the hypochlorite is exhausted, colour formation sets in, and the product must be subsequently purified. When the operation is correctly carried out, the product is obtained as a pale yellow precipitate, sparingly soluble in water or alcohol. It was purified by several extractions with boiling dilute alcohol (30 per cent.), dried, and recrystallized from alcohol. The product separated in colourless plates, which melted at decomposition at 299—300°. Its analysis and properties indicate that it is 4:4'-*dinitrostilbenic*,yl-2:2'-dicarboxylic acid (4:4'-*dinitrophenylglyoxalic* 2:2'-dicarboxylic acid),



Found, C = 53.1, 52.9, 53.5; H = 3.51, 3.28, 3.38; N = 8.67, 7.7.

$\text{C}_{18}\text{H}_{11}\text{O}_7\text{N}_2$  requires C = 53.33; H = 3.33; N = 7.77 per cent.

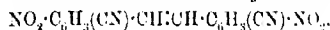
It is not oxidised by permanganate in cold pyridine solution, nor in cold dilute aqueous solution.

We have not yet obtained the corresponding stilbene derivative in pure state, although in several of our experiments, in which quite different conditions from the above were employed, a product was obtained which gave the reactions of a stilbene compound. The melting point of this substance was about 270°. It is reduced to a crimson red compound on adding phenylhydrazine or dextrin to its aqueous solution rendered alkaline with sodium hydroxide.

#### *Action of Caustic Alkalis and Air on p-Nitro- $\sigma$ -toluidine.*

The nitrile was prepared from *p*-nitro- $\sigma$ -toluidine by Sandmeyer reaction, and purified by recrystallisation from alcohol. It was a pale yellow needles which melted at 103°. On adding a solution of potash or strong aqueous potassium or sodium hydroxide to an alcoholic solution of the nitrile, excluding air by a current of hydrogen, a brilliant deep blue coloration is produced. This coloration after some minutes slowly changes to violet, and, if air is admitted, it quickly becomes brown, and a dark tarry precipitate is deposited. The blue compound therefore, like other members of this class, is extremely unstable. Since its isolation was impossible, it was at once submitted to oxidation. Both air and sodium hypochlorite were employed as oxidising agents, the product in each case being the same. The hypochlorite, however, gave the best results. Ten grams of the nitrile were dissolved in 30 c.c. of warm pyridine and filtered, with 300 c.c. of alcohol. To the cold solution were added 100 c.c. of sodium hypochlorite (1.75 per cent. active chlorine). It was immediately by 60 c.c. of strong aqueous sodium hydroxide. The mixture became warm, and a precipitate separated. This was immediately collected by the aid of the pump, and washed with

in 95% alcohol. The crude product was a pale yellow, granular substance, which melted above 200°. For purification, it was recrystallised several times from nitrobenzene and glacial acetic acid. It proved to be 4:4'-dinitro-2:2'-diacyanostilbene,



This compound is sparingly soluble in nitrobenzene, chloroform, or glacial acetic acid, moderately so in pyridine, and almost insoluble in alcohol. It crystallises from glacial acetic acid in small, indistinct, colourless crystals, which melt with decomposition at about 258°. Analysis gave the following results:

Calcd. C=60.9, 60.0, 60.2; H=2.75, 2.5, 2.39; N=17.50, 17.87.

Found.  $\text{H}_2\text{O}_4\text{N}_4$  requires C=59.9; H=2.52; N=17.51 per cent.

This substance at once decolorises permanganate in a cold pyridine solution. On reduction in cold alcoholic solution by addition of sodium hydroxide and a drop of phenylhydrazine, it is reconverted to the deep blue nitrosostilbene from which it is derived.

We have not been able to isolate a second isomeric form. Attempts to convert the nitrile into the carboxylic acid were also unsuccessful, owing to the occurrence of by-reactions on heating with mineral acids.

We desire to express our thanks for a grant from the Chemical Society Research Fund, by which a portion of the expense of this research has been defrayed.

DEPARTMENT OF TINTORIAL CHEMISTRY,  
THE UNIVERSITY,  
LEEDS.

### CV. *The Replacement of Alkyl Radicles by Methyl in Substituted Ammonium Compounds.*

By HUMPHREY OWEN JONES and JOHN ROBERTSLAW HILL.

As shown by one of us (Proc., 1901, 17, 205) that dibenzyl- and quaternary ammonium compounds containing the methyl and benzyl groups, when heated with methyl iodide, yielded benzyl iodide and phenyltrimethylammonium iodide. No other alkyl iodide was tried, namely, ethyl, propyl, isobutyl, and allyl iodides, and it seemed to effect this displacement of the methyl group, and it could be shown that other groups were displaced by methyl (at this time these compounds were not examined). Later (Trans., 1905, 87,

1726), it was found that the allyl group is displaced from *isopropylaniline* by methyl iodide in the cold, and the benzyl group from *isobutylaniline*.

At this time, it seemed that the allyl and benzyl groups were the only ones that could be replaced by the methyl group, since these are the only compounds containing these radicals racemised readily, and also their iodides have the greatest capacity for forming addition, and also their iodides have the greatest capacity for reacting with aromatic tertiary amines, the conclusion that the displacement was dependent on their common properties was again justified.

This displacement of benzyl and allyl groups by methyl was found to be general, as proved by the following transformations, in addition to those already mentioned, which were found to take place when the first-mentioned compound was heated to 100° with methyl iodide alone or with methyl iodide and alcohol or chloroform.

Phenylbenzylmethylisocyanylammonium iodide  $\rightarrow$  phenylbenzylisocyanylammonium iodide, phenylbenzylmethylisopropylammonium iodide  $\rightarrow$  phenyldimethylisopropylammonium iodide, phenylallylammonium iodide  $\rightarrow$  phenyltrimethylammonium iodide, phenyldiallylammonium iodide  $\rightarrow$  phenyltrimethylammonium iodide, phenylmethylisocanylallylammonium iodide  $\rightarrow$  phenylmethylallylammonium iodide.

Ethyl, propyl, *isobutyl*, and *isocanyl* iodides, when heated with benzyl and allyl compounds, did not effect any displacement, and the colour of allyl or benzyl iodide was always noticeable.

In 1906, some anomalous results were obtained while attempting to prepare a series of compounds containing the phenyl, methyl, ethyl groups together with propyl, *isopropyl*, *isobutyl*, and *isocanyl* groups. Ethylisocyanylaniline and methyl iodide were found to combine slowly in the cold, and the resulting product was found to be phenylmethylethylisocanylammonium iodide.

Ethylisopropylaniline and methyl iodide reacted very slowly in the cold, but eventually deposited a crystalline solid which, after repeated crystallisations, melted at 167–168°. It was found to be identical with phenyldimethylisopropylammonium iodide (m.p. 168°), prepared from methylisopropylaniline and methyl iodide. It was evident therefore that the ethyl group was in this case displaced by methyl in the cold.

Ethylpropylaniline and methyl iodide reacted slowly, depositing a gum which became crystalline on standing; after recrystallisation the following numbers were obtained on analysis:

Found, C = 45.12, 45.4; H = 6.39, 6.4.

$\text{MeEtPh}(\text{C}_3\text{H}_7)\text{NI}$  requires C = 47.2; H = 6.56 (calculated).

$\text{Me}_2\text{Ph}(\text{C}_3\text{H}_7)\text{NI}$  „ C = 45.12; H = 6.41 (observed).

A similar displacement of the ethyl group has evidently taken place here. This compound and the product from methylpropylaniline and methyl iodide are very soluble, and difficult to recrystallise and purify; hence their absolute identity has not yet been established.

Later it was found that the series of substituted *p*-bromoanilines already described (Hill, *Proc. Camb. Phil. Soc.* 1907, 14, 166) all heated at 100° with methyl iodide and gave *p*-bromophenyltrimethylammonium iodide. This compound is very easy to isolate and purify, even when formed in quite small quantities, on account of its low solubility in alcohol, its characteristic appearance, and melting point of 200°, a melting point which is higher than that of any of the trimethylammonium iodides derived from this series of amines.

*p*-Bromomethylethylaniline or *p*-bromophenyldimethylethylammonium iodide and the corresponding propyl, *isopropyl*, *n*-butyl, and *isobutyl* compounds were found to give some *p*-bromophenyltrimethylammonium iodide after heating at 100° for two hours in a sealed tube with excess of methyl iodide; the *isobutyl* compound seemed to be completely transformed, whilst the ethyl, propyl, and *n*-butyl compounds yielded a moderate quantity of the trimethyl compound.

The *isoamyl* compound, however, seemed to react much less readily, and at first it was thought that no action had taken place; but after prolonged heating, the trimethyl compound was detected: *p*-bromophenylmethyl*isoamyl*ammonium iodide yielded the trimethyl compound in somewhat larger quantity.

It is clear therefore that the six saturated hydrocarbon radicals considered above behaved in the same way as the benzyl and allyl compounds; that they were not always so readily nor so completely displaced by methyl, as the benzyl and allyl groups.

Attention was now directed to the corresponding series of phenyl compounds to determine whether they behaved in the same way as the *n*-phenyl derivatives. Phenyldimethylethylammonium iodide and the corresponding propyl, *isopropyl*, *isobutyl*, and *isoamyl* compounds were heated with methyl iodide and examined for phenyltrimethylammonium iodide. This compound is easy to identify on account of its slight solubility, which, however, is much greater than that of the corresponding bromo compound, and its behaviour on heating when it volatilises at 229°. All the compounds, except the *isoamyl* derivative, were found to give phenyltrimethylammonium iodide, and even after prolonged heating none could be obtained from the *isoamyl* compound.

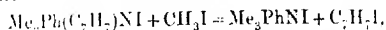
It should be noted, however, that phenylbenzylmethyl*isoamyl*ammonium iodide yielded some phenyltrimethylammonium iodide after heating with excess of methyl iodide.



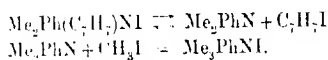
Here, the ease with which a radicle was displaced seemed to depend with increasing molecular weight, except that the isobutyl group appeared to be more readily replaced than the propyl; but the order with which displacement took place in all cases was distinctly different from that in the corresponding bromo-compounds. Phenylbenzylisopropylammonium iodide (Trans., 1905, 87, 135) was found to be displaced from trimethyl compound with difficulty, like the corresponding isobutyl derivative.

It seems probable that the difference between the isobutyl and other groups as regards the ease with which they are replaced is only one of degree.

The displacement of alkyl radicles by methyl could take place in one of two quite distinct ways: (1) by direct action between methyl iodide and the ammonium iodide, thus:



or (2) partial dissociation into tertiary amine and an alkyl iodide might occur in the methyl iodide solution; then the methyl iodide being present in great excess would react with the tertiary amine to form an ammonium iodide until equilibrium was established in solution, thus:



On consideration, the latter view appears the more probable, for we know that the dissociation postulated does occur in chloroform solution and results in gradual racemisation of active amine iodides. That this same dissociation also occurs in solutions of alkyl iodides was shown by examining solutions of 1:1:1:1 benzylmethylisopropylammonium iodide (Thomas and Jones, 1905, 89, 285) in methyl iodide and in ethyl iodide. The salt is extremely sparingly soluble in the iodides, but the addition of a few drops of alcohol enabled a solution to be prepared with a rotation great enough for the changes to be observed.

In methyl iodide:

Initial rotation,  $-0.57^\circ$ ; after six hours,  $-0.32^\circ$ ; after twelve hours,  $-0.14^\circ$ ; after twenty-four hours,  $-0.11^\circ$ ; after thirty hours,  $-0.03^\circ$ ; after thirty-six hours, inactive.

In ethyl iodide:

Initial rotation,  $-0.62^\circ$ ; after six hours,  $-0.40^\circ$ ; after twelve hours,  $-0.12^\circ$ ; after thirty hours,  $-0.07^\circ$ ; after thirty-six hours, inactive.

Hence this iodide racemises in methyl and in ethyl iodide *at least* at practically the same rate as in chloroform (compare Thomas and

It follows, therefore, that a dissociation into tertiary amine and alkyl iodide must take place in the case of compounds containing these groups besides benzyl and allyl. Unfortunately, up to the present time, no optically active nitrogen compound is known which does not contain either the benzyl or allyl group together with methyl, otherwise this dissociation could be shown by their auto-replacement.

Ease of replacement would then depend on the extent to which the dissociation into alkyl iodide and tertiary amine occurred. It is probable that the order of the alkyl radicles as regards extent of dissociation would be the same as that for ease of addition. Taking Winkler's values for the percentage amount of ammonium salt formed from these alkyl iodides and dimethylaniline in fifty-three cases (*Stereochemie des fünfwertigen Stickstoffs*, 1899, 21)\* namely, allyl, 84; ethyl, 15; *n*-propyl, 28; isopropyl, 5; *n*-butyl, 17; isobutyl, 16; isamyl, 2.5; allyl, 93; benzyl, 83, we see that the ease of replacement, which is determined presumably by the extent of the dissociation, is roughly in the same order as the ease of formation of quaternary salt by the alkyl iodide in question.

There is, however, an apparent exception in the case of the isamyl compound, which we find to be the most difficult to displace, more difficult than the isobutyl group, yet its iodide appears to combine with dimethylaniline more readily than the latter.

We therefore examined this point further by allowing mixtures of dimethylaniline and equivalent quantities of ethyl iodide, isobutyl iodide and isamyl iodide to remain for one month at the ordinary temperature. The much longer time was allowed in order to avoid such large percentage error from the solubility of the salt in the mixture of amine and iodide, which, when very small quantities such as Winkler obtained (0.15–0.8 gram) are concerned, must exert a marked influence on the quantitative results. One-twentieth of a gram-molecule of each mixture was taken, and after standing one month the iodide was separated, dried between filter paper, and weighed (the isobutyl compound was crystalline), and found to be 23.6 per cent. for ethyl, 2.0 per cent. for isobutyl, and 1.3 per cent. for isamyl. Hence it would appear that the isamyl iodide has not, at least, a greater reaction velocity than the isobutyl.

Methyl iodide comes third in order of rapidity of reaction with dimethylaniline, and it is therefore surprising to find that it is the one least capable of replacing all the others; the explanation of this is probably to be found in the very small solubility of the methyl iodide compared with the others, which also accounts for the peculiar ease with which replacement takes place in the *p*-bromodimethylaniline in the phenyl series. The solubilities of the substituted

ammonium iodides in alcohol at the ordinary temperature, expressed in grams in 100 grams, are as follows:

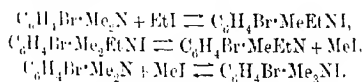
		<i>p</i> -Bromophenyltrimethylammonium iodide	
	Solubility.	Melting point.	Solubility.
		226°	
		(volatilises)	
Methyl .....	1.1		0.12
Ethyl .....	45.1	136	1.15
Propyl .....	11.8	168	3.30
Isopropyl .....	24.1	155-156	5.69
Isobutyl .....	18.4	138	2.38
Isopentyl .....	2.7	165	—

It therefore appears that the ease with which a radicle is displaced by methyl is dependent on two factors; first, the amount of dissociation into tertiary amine and alkyl iodide, of which the former is the formation of the salt from alkyl iodide and amine may be regarded as a measure, and secondly, the solubility of the ammonium salt, in which the group is to be displaced. The slight solubility of the trimethyl compound enables this to separate from the solution and to be removed from the sphere of action.

The ready solubility of the *isobutyl* compound of the *p*-bromophenyl series probably accounts for the fact that this group is more readily displaced than all the others.

On the view expressed above, that the extent of the dissociation is determined by the velocity of addition of the alkyl iodide to the tertiary amine, ammonium salts containing the methyl group should dissociate into amine and methyl iodide to quite a considerable extent. That this is actually the case is shown by the following observations. *p*-Bromodimethylaniline was allowed to stand with the iodides of the following radicles, ethyl, propyl, isopropyl, *isobutyl*, and *isopentyl*. At the cold, the reaction was extremely slow, except in the case of the ethyl compound. The solid deposited in this case was found to be chiefly of *p*-bromophenyltrimethylammonium iodide. At 60°C. the other four alkyl radicles also yielded a considerable quantity of the trimethyl compound.

It would appear that the following scheme is the probable explanation of these results:



The quaternary salt first formed is dissociated in two different ways, so that in the solution we have an equilibrium between the alkyl iodides and two tertiary amines. The very small solubility of the trimethyl compound then determines the separation of the same from the solution. A dissociation of ammonium salts into tertiary

and two alkyl iodides on heating has been observed by Wedekind (*Ber.*, 1902, **35**, 766).

The results may be summarised as follows: the groups, allyl, benzyl, *allyl*, *isobutyl*, propyl, *isopropyl*, and *isoamyl*, are displaced from ammonium salts by the methyl group on treating with methyl iodide, sometimes in the cold, more usually on heating. The displacement takes place owing to the salt dissociating in methyl iodide solution into tertiary amines and alkyl iodides; an equilibrium is set up between the dissociated amines, iodides, and the methyl iodide, and, since in each case the trimethyl compound is much less soluble than the other, this separates, and so is found in much greater quantity than the other in the solid product.

The order given is roughly that of the ease of displacement of these radicals, which is determined by the extent of the dissociation and the solubility of the ammonium salt in question. The *isoamyl* group is the most difficult to displace.

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$C_{26}H_{42}O_2N_2S_2$ .....	801	$C_{22}H_{17}O_3N_3$ .....	1291
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$C_{26}H_{40}O_4I_2Zn$ .....	900	$C_{22}H_{16}O_3N_2S$ .....	803
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$C_{21}H_{14}O_8$ .....	1580	$C_{22}H_{40}O_{14}N_{10}Cu$ .....	21
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$C_{21}H_{24}O_6$ .....	570	$C_{22}H_{41}O_4Nssi$ .....	734
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$C_{21}H_{17}O_4N_6S$ .....	114	$C_{23}H_{25}ON$ .....	700
$C_{21}H_{19}O_3NS$ .....	1621	$C_{23}H_{20}ON_3S$ .....	924
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		$C_{25}H_{22}N_2$ .....	

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1915	$\text{C}_2\text{H}_2\text{O}_4$	1294	$\text{C}_{24}\text{H}_{36}\text{ON}_2\text{Cl}$	1245	$\text{C}_{40}\text{H}_{36}\text{N}_6\text{Cl}_6\text{Pt}$
571	$\text{C}_2\text{H}_2\text{O}_4$	1930	$\text{C}_{24}\text{H}_{36}\text{N}_2\text{Cl}_6\text{Pt}$	1242	$\text{C}_{40}\text{H}_{36}\text{N}_2\text{Cl}_6\text{Pt}, 2\text{H}_2\text{O}$
1239	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	98	$\text{C}_{24}\text{H}_{48}\text{O}_3\text{N}_2\text{S}$		<b>C<sub>41</sub> Group.</b>
1322	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	1318	$\text{C}_{24}\text{H}_{34}\text{O}_3\text{N}_2\text{Cl}_6\text{Pt}$	1777	$\text{C}_{41}\text{H}_{22}\text{O}_{11}$
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1043	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{H}_2$	1624	$\text{C}_{23}\text{H}_{22}\text{O}_4\text{N}_2$		<b>C<sub>44</sub> Group.</b>
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707	$\text{C}_2\text{H}_2\text{O}_4$	1432, 1433	$\text{C}_{23}\text{H}_{26}\text{O}_2\text{N}_2$	229	$\text{C}_{44}\text{H}_{40}\text{O}_7\text{N}_2\text{S}_2\text{Si}_2, 4\text{H}_2\text{O}$
1238	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	347	$\text{C}_{23}\text{H}_{40}\text{O}_6\text{N}_3$		<b>C<sub>46</sub> Group.</b>
419	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	350	$\text{C}_{23}\text{H}_{22}\text{O}_6\text{N}_2\text{Cl}$	527	$\text{C}_{46}\text{H}_{36}\text{O}_{16}\text{S}_4\text{Cr}_2$
199	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	350	$\text{C}_{23}\text{H}_{40}\text{O}_{10}\text{N}_3\text{P}$	527	$\text{C}_{46}\text{H}_{36}\text{O}_8\text{Cl}_6\text{S}_4\text{Pt}$
1349	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	349, 350	$\text{C}_{23}\text{H}_{40}\text{O}_{10}\text{N}_3\text{P}, \text{H}_2\text{O}$		<b>C<sub>50</sub> Group.</b>
1294	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$		<b>C<sub>26</sub> Group.</b>	1623	$\text{C}_{50}\text{H}_{44}\text{O}_{12}\text{N}_2\text{Cr}_2$
1979	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	96	$\text{C}_{26}\text{H}_{40}\text{O}_{14}\text{N}_4\text{H}_2\text{O}$	903	$\text{C}_{50}\text{H}_{40}\text{O}_2\text{N}_2\text{Cl}_4\text{Fe}$
804	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{S}_2$	477	$\text{C}_{26}\text{H}_{20}\text{O}_{18}\text{S}_6\text{Ce}_2, 23\text{H}_2\text{O}$		<b>C<sub>52</sub> Group.</b>
1235, 1236, 1237	$\text{C}_2\text{H}_2\text{N}$	476	$\text{C}_{26}\text{H}_{20}\text{O}_{22}\text{S}_6\text{Ce}_2, 12\text{H}_2\text{O}$	523	$\text{C}_{52}\text{H}_{40}\text{O}_{12}\text{S}_2\text{Cr}_2$
1511	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{S}$	476	$\text{C}_{26}\text{H}_{20}\text{O}_{22}\text{S}_6\text{Ce}_2, 17\text{H}_2\text{O}$	527	$\text{C}_{52}\text{H}_{40}\text{O}_6\text{Cl}_6\text{S}_4\text{Pt}$
1238	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{S}$	96	$\text{C}_{26}\text{H}_{20}\text{O}_8\text{N}_2\text{Br}_2, \text{H}_2\text{O}$		<b>C<sub>54</sub> Group.</b>
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1357, 1391	$\text{C}_2\text{H}_2\text{O}_4$	900	$\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_6\text{Co}$	1239	$\text{C}_{54}\text{H}_{20}\text{O}_4\text{N}_4\text{Cl}_6\text{Pt}$
1343	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	477	$\text{C}_{26}\text{H}_{20}\text{O}_{18}\text{N}_6\text{Ce}_2, 16\text{H}_2\text{O}$		<b>C<sub>56</sub> Group.</b>
1346	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	97	$\text{C}_{26}\text{H}_{40}\text{O}_8\text{N}_2\text{Cl}_6\text{Pt}$	1236, 1237	$\text{C}_{56}\text{H}_{40}\text{N}_2\text{Cl}_6\text{Pt}, 12\text{H}_2\text{O}$
1344	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	97	$\text{C}_{26}\text{H}_{40}\text{O}_8\text{N}_2\text{Cl}_6\text{Pt}, \text{H}_2\text{O}$	1235, 1236	$\text{C}_{56}\text{H}_{40}\text{N}_2\text{Cl}_6\text{Pt}, 2\text{H}_2\text{O}$
1345, 1350	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	95	$\text{C}_{26}\text{H}_{40}\text{O}_{10}\text{N}_2\text{Cl}_6\text{Pt}, 2\text{H}_2\text{O}$	1235	$\text{C}_{56}\text{H}_{40}\text{N}_2\text{Cl}_6\text{Pt}, 3\text{H}_2\text{O}$
704	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$		<b>C<sub>17</sub> Group.</b>	1238	$\text{C}_{56}\text{H}_{40}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}, 3\text{H}_2\text{O}$
1511	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{S}$	351	$\text{C}_{27}\text{H}_{40}\text{O}_{10}\text{N}_2$	1238	$\text{C}_{56}\text{H}_{40}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}, 3\text{H}_2\text{O}$
	<b>C<sub>2</sub> Group.</b>	1980	$\text{C}_{27}\text{H}_{44}\text{O}_2\text{N}_2$		<b>C<sub>60</sub> Group.</b>
1387, 1392	$\text{C}_2\text{H}_2\text{O}_4$		<b>C<sub>28</sub> Group.</b>	476	$\text{C}_{60}\text{H}_{42}\text{O}_{22}\text{S}_6\text{Ce}_2, 20\text{H}_2\text{O}$
72, 77	$\text{C}_2\text{H}_2\text{O}_4$	1917	$\text{C}_{28}\text{H}_{42}\text{O}_4\text{H}_2\text{O}$	477	$\text{C}_{60}\text{H}_{30}\text{O}_{22}\text{S}_6\text{Ce}_2, 20\text{H}_2\text{O}$
539	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	1661	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{Cl}_6\text{Pt}$	32\text{H}_2\text{O}	
902	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{Ce}$	1662	$\text{C}_{28}\text{H}_{26}\text{O}_2\text{N}_2\text{Cl}_2\text{Cr}$	477	$\text{C}_{60}\text{H}_{48}\text{O}_{12}\text{N}_6\text{S}_6\text{Ce}_2, 2\text{H}_2\text{O}$
901	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{S}_2\text{Fe}$	1664, 1665	$\text{C}_{28}\text{H}_{20}\text{O}_7\text{N}_2\text{Br}_2\text{Cr}_2$		<b>C<sub>70</sub> Group.</b>
901	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{Cl}$	1121	$\text{C}_{28}\text{H}_{30}\text{O}_{10}\text{Cl}_6\text{S}_2\text{Pt}$	1624	$\text{C}_{70}\text{H}_{32}\text{O}_{12}\text{N}_2\text{Cr}_2$
	<b>C<sub>1</sub> Group.</b>	1937	$\text{C}_{28}\text{H}_{24}\text{ON}_2\text{Cl}_6\text{Pt}$		<b>C<sub>72</sub> Group.</b>
1665	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2\text{Br}$	1938	$\text{C}_{28}\text{H}_{26}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$	351	$\text{C}_{72}\text{H}_{64}\text{O}_{18}\text{N}_{10}$
	<b>C<sub>2</sub> Group.</b>	1663	$\text{C}_{28}\text{H}_{26}\text{O}_7\text{N}_2\text{Cl}_2\text{Br}_2\text{Cr}_2$		<b>C<sub>84</sub> Group.</b>
1295	$\text{C}_2\text{H}_2\text{O}_4$		<b>C<sub>29</sub> Group.</b>	1623	$\text{C}_{84}\text{H}_{70}\text{O}_6\text{N}_4\text{Cl}_6\text{Pt}$
1146	$\text{C}_2\text{H}_2\text{O}_4$	1918	$\text{C}_{29}\text{H}_{44}\text{O}_4$		<b>C<sub>88</sub> Group.</b>
1295	$\text{C}_2\text{H}_2\text{O}_4$	1240	$\text{C}_{29}\text{H}_{22}\text{O}_{16}\text{N}_8$	1625	$\text{C}_{88}\text{H}_{70}\text{O}_6\text{N}_4\text{Cl}_6\text{Pt}$
1145	$\text{C}_2\text{H}_2\text{O}_4$		<b>C<sub>30</sub> Group.</b>		<b>C<sub>90</sub> Group.</b>
1145	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	1108, 1112	$\text{C}_{30}\text{H}_{22}$	1624	$\text{C}_{90}\text{H}_{80}\text{O}_{18}\text{N}_4\text{Cl}_6\text{Pt}$
	<b>C<sub>1</sub> Group.</b>	1236, 1237	$\text{C}_{30}\text{H}_{22}\text{O}_{14}\text{N}_7$		
1237	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$	1238	$\text{C}_{30}\text{H}_{22}\text{O}_{15}\text{N}_7$		
1323	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$				
1295	$\text{C}_2\text{H}_2\text{O}_4\text{N}_2$				
	<b>C<sub>1</sub> Group.</b>				

# ERRATA.

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Page	Line	
37	5	for " $O_2C_6H_4Br_2N_2$ " read " $O_2C_6H_4Br_2N_2$ ."
256	13*	" " $C_{16}H_{19}O_8N_2$ " read " $C_{16}H_{19}O_8N_2$ ."
335	6	" " $C_{16}H_{19}O_8N_2$ " read " $C_{16}H_{19}O_8N_2$ ."
350	7	" " $C_{16}H_{19}O_8N_2$ " read " $C_{16}H_{19}O_8N_2$ ."
354	2	" "ay" read "ad."
425	18	" "5:1-Hydroxy." read "1-Hydroxy."
548	6*	" " $C_9H_{10}O_2$ " read " $C_9H_{10}O_2$ ."
763		transpose Fig. 3 to page 767.
767		Fig. 2 " 763.
920	15*	for "aa-carboxyphenylphenylthiocarbonate" read "aa-carboxyphenylphenylthiocarbamate"
1375	2*	" " $t_1$ " read " $t_2$ ."
1376	2*	and 11* in equation, for " $t_1$ , $t_2$ , and $t_3$ " read " $z_1$ , $z_2$ , and $z_3$ " respectively.
1377		in equation (19), in right-hand expression, for " $=$ " read " $=$ " and equation (21a), in left-hand expression, for " $k$ " read " $k_2$ ."
1441	2*	for " $C_8H_7O_4N$ " read " $C_8H_{11}O_4N$ ."
1531	18	" " $B$ " read " $\beta$ ."
1591	2	" "7(10)-amino-1-naphthacenequinone" read "7(10)-amino-1-hydroxynaphthacenequinone."
1640	4*	" " $C_{16}H_{19}O_8$ " read " $C_{16}H_{19}O_8$ ."
1662	4*	" " $C_{16}H_{19}NClBr_2$ " read " $C_{16}H_{19}NClBr_2$ ."
1749	2*	" "mostly" read "only."
1750	6	" "Serturnier" read "Sertuerner."
1750	7	" "ten years" read "decades."
1752	17*	" "biose" read "glycollaldehyde."
1762	16*	" "Mackenzie" read "A. McKenzie."
1755	7	" "no less than" read "some."
1755	10	" "as well as" read "of."
1756	2	delete the sentence "I may mention . . . the yeast cell."
		NOTE.—Buchner has recently informed me that his statement ( <i>Oesterreich. Chem. Zeit.</i> , 1898, No. 7), from which the above conclusion could be drawn, was meant in a different sense.—E. F.
1760	6	for "H. Kossel" read "A. Kossel and H. D. Dakin."
1761	26	after "acid" insert "ornithine, oxyproline, and isoleucine."
1763	15	for "ten years" read "decades."
1764	6*	" "ten years" read "decades."
1765	2	" "blood" read "flower."
2034	20 & 21	" " $3Hg_2O \cdot N_2O_3$ " read " $3Hg_2O \cdot N_2O_3$ ."
2034	26	" " $Hg_2O \cdot 2Hg_2O \cdot N_2O_3$ " read " $Hg_2O \cdot 2Hg_2O \cdot N_2O_3$ ."
2035	9, 10 & 21	for " $Hg \cdot Ag$ " read " $Hg', Ag$ ."
2035	{ 2, 4, 6, 9, 21, 22 & 24 }	" " $Hg' \cdot Ag$ " read " $Hg', Ag$ ."

\* From bottom.

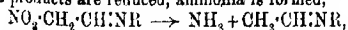
## Organic Chemistry.

**Preparation of Tetranitromethane.** CONRAD CLAESSEN (U.R.P. 184229).—The production of tetranitromethane from nitroform, which is itself obtained with difficulty from explosive substances such as mercury fulminate, is too dangerous to admit of this process being employed on a large scale. It is now found that the aromatic hydrocarbons and their nitro-derivatives when warmed with a mixture of nitric-sulphuric acid (40%  $\text{H}_2\text{SO}_4$ , 60%  $\text{HNO}_3$ ) and fuming sulphuric acid (50%  $\text{SO}_3$ ) furnish a large amount of tetranitromethane; a yield of 5% on the weight of the organic substance being sometimes obtained. Nitrobenzene when gradually heated with excess of the acid mixture to  $120^\circ$  is decomposed, giving rise to tetranitromethane and a large amount of nitrous fumes. G. T. M.

**Improved Method for the Preparation of Alkyl Chlorides.** WILLIAM M. DEHN and GRANT T. DAVIS (*J. Amer. Chem. Soc.*, 1907, 29, 1328—1334).—A method is described for the preparation of alkyl chlorides by the action of phosphorus trichloride on alcohols in presence of zinc chloride. Propyl chloride has been obtained in a yield amounting to 94% of the theoretical by the use of anhydrous zinc chloride. It has been found that, if a solution of zinc chloride (b.p.  $150$ – $160^\circ$ ) is used instead of the anhydrous salt, the yield of propyl chloride is decreased, but that in the case of isobutyl and amyl chlorides larger yields (85% and 88%, respectively) are produced. The reaction takes place in accordance with the equation:  $3\text{ROH} + 2\text{PCl}_3 + \text{ZnCl}_2 = \text{Zn}(\text{H}_2\text{PO}_3)_2 + 6\text{RCl} + 2\text{HCl}$ . Evidence has been obtained, however, of the formation of complex intermediate products.

By the action of stannic chloride on propyl alcohol, an additive compound, b. p.  $148^\circ$ , is obtained. E. G.

**Constitution of Methazonic Acid.** WILHELM MEISTER (*Ber.*, 1907, 40, 3435—3449. Compare Dunstan and Goulding, *Trans.*, 1907, 77, 1262; Scholl, *Abstr.*, 1901, i, 359).—Methazonic acid behaves as a primary nitro-compound, since it gives the nitrolic acid reaction and Konowaloff's reaction, and hence contains the grouping  $\text{CH}\cdot\text{NO}_2$ . It reacts with primary aromatic amines and hydrazines, yielding products which also contain the primary nitro-group. These products are formed by the replacement of  $\text{NHO}$  by  $\text{NR}$ , and hydroxylamine is also formed. The reactions are most readily explained by the presence of the oximino-group in methazonic acid, and the formula thus arrived at is  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}=\text{N}\cdot\text{OH}$ . When the nitrosation products are reduced, ammonia is formed,



and the residue, when distilled with acid, yields an amine and acet-



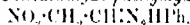
aldehyde,  $\text{CH}_3\text{CH:NR} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO} + \text{NH}_2\text{R}$ . The reaction resembles Schiff's bases.

An isonitro formula,  *$\beta$ -isonitroacetaldoxime*,  
 $\text{OH}\cdot\text{NO}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ ,

is also possible. The formation and reactions of methazonic acid are discussed from the point of view of the new formula.

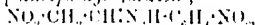
Attempts have been made to synthesise methazonic  $\beta$ -chloro- or  $\beta$ -iodo-acetaldoxime and silver nitrite, but without success.

Methazonic acid and phenylhydrazine in the presence of chloric acid yield  *$\beta$ -nitroacetaldehyde phenylhydrazone*,



It may be crystallised in small amounts (0.1–0.2 gram) in petroleum and forms glistening, white plates, m. p. 74–75°. Kept in closed vessels, it rapidly decomposes, but can be kept in open vessels if protected from sunlight. It dissolves in the nitrolic acid reaction, and yields precipitates with the heavy metals.

*Nitroacetaldehyde- $p$ -nitrophenylhydrazone*,



forms orange-brown flakes which decompose at 141–142°.

*$\beta$ -Nitroethylidene- $p$ -chloroanil*,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}$ , from the acid and  $p$ -chloroaniline, crystallises from light petroleum in minute, canary-yellow needles decomposing at about 150°. The corresponding *p*-nitroanil,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , from chloroform in shimmering, yellow needles which melt at about 185°.

*$\beta$ -Nitroethylideneanil*,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}$ , forms yellow needles, m. p. 94–95° after sintering at 90°.

When hydrolysed with alkali, the  $p$ -chloroanil yields  $p$ -chloroaniline, ammonia, hydrogen cyanide, formic acid, methazonic acid, and carbon dioxide. With acids, the same compound yields the same products with the exception of ammonia and methazonic acid, hydrogen being formed in place of ammonia.

**The Series Resulting from the Methylation of Alcohol, with Regard to the Aptitude for Isomerism of the Halide Ethers.** LOUIS HENRY (*Compt. rend.* 1906, 547–549). A comparison is given of the facility with which halide ethers derived from the ethyl halides,  $\text{CH}_3\text{CH}_2\text{X}$ , isomerise (1) in the  $\text{CH}_3$  group exclusively; (2) in the  $\text{CH}_2$  group exclusively, and (3) in the  $\text{CH}_3$  and  $\text{CH}_2\text{X}$  group simultaneously. Hydrogen by methyl, undergo isomeric change. (1) The primary derivatives change into the isocompounds, the *isobutyl* and *tert*-butyl, and the triethylethyl halides change readily into the tertiary amyl derivatives. (2) The secondary *tert*-butyl halides do not change isomerically. (3) The tertiary butyl halides are stable, but the methylisopropyl compounds and methyl *tert*-butyl carbinol halide ethers are easily changed into tertiary halide derivatives. The tertiary halide compounds are stable. This review reveals the fact that isomeric change occurs in

and the less the number of hydrogen atoms combined with the carbon atom attached to the halide-ether chain. Thus the abundant presence of hydrogen confers stability on the polycarbon chains.

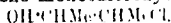
E. H.

**Beeswax. II. Psyllostearyl Alcohol as a Constituent.** HANS EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1907, 53, 365—369. *Chem. Abstr.*, 1898, i, 617; 1901, i, 358).—By the use of improved methods, the surmise that psyllostearyl alcohol is present in beeswax was confirmed. The wax of *Bombus terrestris* was used in the present instance, acetone being used as the extracting agent. W. D. H.

**Propylene Oxide,**  $\begin{matrix} \text{CHMe} \\ | \\ \text{CH}_2 \end{matrix} \text{---} \text{O}$ . LOUIS HENRY (*Compt. rend.*, 1907, 145, 453—456).—The action of magnesium ethyl bromide on propylene oxide has been studied in order to ascertain whether it gives rise to a product by simple addition as in the case of ethylene oxide (this vol., i, 745), or whether isomeric change initially occurs as with dimethylethylene oxide (this vol., i, 817) and *as*-dimethylethylene oxide (this vol., i, 744). The product actually obtained was methyl propylcarbinol,  $\text{CHMePr}\cdot\text{OH}$ , which was identified by means of the semicarbazone (m. p. 100°) of the ketone,  $\text{COMePr}$ , from an oxidation. The behaviour of propylene oxide is thus entirely that of ethylene oxide; the substitution of a single methyl group is not sufficient to bring about the possibility of undergoing isomeric change which exists in the dimethylated derivatives. It is also observed that epichlorohydrin on combining with magnesium ethyl bromide gives  $\alpha$ -chloro- $\gamma$ -hydroxy- $\beta$ -ethylpropane,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ .

W. A. D.

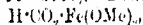
#### Secondary Butylene Monochlorohydrin,



LOUIS HENRY (*Compt. rend.*, 1907, 145, 498—499).—*Secondary* *butylene monochlorohydrin* (*γ*-chloro *sec. butyl alcohol*) is prepared by the action of hypochlorous acid to *sd*-dimethylethylene obtained by the action of alcoholic potash on *sec. butyl iodide*,  $\text{CHMeEtI}$ ; it is a colourless, somewhat viscous liquid, soluble in about 15 vols. of water (*d*<sub>4</sub> 1.105,  $\mu$  1.44376, mol. refraction 26.05 (calc. 26.98), b. p. 57° at 753 mm. It is very sensitive to alkalis and alkali carbonate being converted into *sd*-dimethylethylene oxide,  $\begin{matrix} \text{CHMe} \\ | \\ \text{CHMe} \end{matrix} \text{---} \text{O}$ .

W. A. D.

**Crystalline Iron Methoxides.** KARL A. HOFMANN and GERTHER (*Ann. Ber.*, 1907, 40, 3764—3766).—*Dimethoxyferric formate*,



and *dimethoxyferric acetate*,  $\text{Me}\cdot\text{CO}_2\cdot\text{Fe}(\text{OMe})_2$ , are obtained by dissolving a wire in formic or acetic acid, evaporating the solution, and treating the residue with methyl alcohol in an atmosphere of carbon dioxide; both form yellow, double-refracting crystals, yield lamellae in contact with a glowing copper spiral, and decompose

gradually in contact with water and immediately with hydrochloric acid, the solution showing the reactions of a ferric salt.

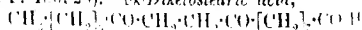
The formation of these compounds depends on the esterification of the basic ferric salts formed intermediately (compare Hofmann and Hochtlen, Abstr., 1905, i, 38).

The substance,  $(\text{MeCO}_2)_2\text{Fe}(\text{OEt})$ , is a red powder, which is obtained by the evaporation in a vacuum of an ethyl-alcoholic solution of ferrous acetate after rapid oxidation in air.

**Some Salts of Glucinum and Zirconium.** SEBASTIANI and E. KURORSKI (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 257). Compare this vol. i, 261.—The salts obtained by the action of organic acids on glucinum carbonate mostly correspond to the formula  $\text{Gl}_2\text{OX}_n$ . They are non-volatile, but most are soluble in benzene, some also in other organic solvents and in water. In the liquid state they are non-conductors of electricity. The following salts are described: *Formate* [the compound  $\text{Gl}(\text{CHO}_2)_2$  was also obtained], *acetate*, *isobutyrate*, *lactate*, and *propionate*. Glucinum also forms compounds of the type  $\text{Gl}_2\text{OX}_n\text{N}_3$  and  $\text{Gl}_2\text{OX}_n\text{N}_4$ . By heating glucinum butyrate with acetyl chloride, the compound  $\text{Gl}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_2\text{H}_5\text{O}_2)_2$  is obtained as a viscous liquid substance, m. p.  $-15^\circ$ , b. p. 551°. Similarly, the compound  $\text{Gl}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_2\text{H}_5\text{O}_2)_2$  was obtained as a crystalline substance, m. p.  $127^\circ$ , b. p. 551°. The normal salts of glucinum with dibasic acids can be obtained readily; the following are described: *succinate*, *citracetate*, *malate*, and *fumarate*. The salts of glucinum are very similar in composition and solubility to the corresponding zirconium salts. *Zirconium propionate*, *valerate*, *crotonate*, and *succinate* are described. The quadrivalency of glucinum is again insisted on; thus the compounds formed by the metals of the fourth group with acetyl chloride are analogous in properties to the corresponding glucinum compounds, whereas the compounds of the metals of the second group are quite different.

**Preparation of Double Lactates containing Antimony.** CHEMISCHER FABRIK VON HEYDEN (AKTIEN-GESELLSCHAFT, PAT. 184202). Antimonyl sulphate, obtained by the action of sulphuric acid on antimonious sulphide, is introduced into a neutral solution of sodium lactate, the solution is concentrated until the excess of sulphate has separated, and the filtrate then evaporated to dryness. The *sodium antimonyl lactate* thus obtained is a soluble double salt which dissolves in water without decomposition. *Calcium antimonyl lactate*, a soluble, crystalline, slightly hygroscopic salt, is obtained by partially replacing sodium lactate by the corresponding calcium salt in the foregoing double decomposition.

**Preparation of *6,8*-Diketostearic Acid.** ANDERSON and SOBEL (D.R.-P. 180226).—*6,8*-Diketostearic acid,



m. p. 106.5°, obtained by oxidising *o*-ketohydroxystearic acid with chromic acid and acetic acids, was crystallised from water and obtained in colourless leaflets soluble in warm alcohol or benzene. With the exception of its sparingly soluble alkali and ammonium compounds, its salts are insoluble in water. This acid behaves as a  $\delta$ -diketone, and owing to this circumstance yields derivatives of technical importance: its *diurime*, m. p. 113–114°, and its *pyrrole* derivative,  $\text{CH}_2=\text{CH}$

$\text{CH}_2=\text{CH}\cdot\text{C}(\text{NH}\cdot\text{C}(\text{CH}_2)_4\text{CO}_2\text{H})_2$ , have been prepared.

G. T. M.

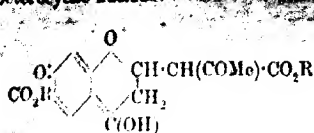
**Xanthophanic Acid.** II. CURT LIEBERMANN and SIMON LINDENBERG, *Ber.*, 1907, 40, 3570–3583. (Compare Abstr., 1906, i, 556).—The products obtained from xanthophanic acid methyl and ethyl ethers have been further investigated. The acid, m. p. 256° (255°; *loc. cit.*), is isolated from the magnesium methoxide “transformation product” of xanthophanic acid methyl or ethyl ether, is shown to be a resacetophenonecarboxylic acid, having probably the annexed structure: the *bromophenylhydrazone* of this,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4(\text{OH})\cdot\text{CMe}(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})$ , crystallises in white needles, m. p. 213°. The acid cannot be esterified by means of alcohol and hydrogen chloride. The methyl ester,  $\text{C}_{15}\text{H}_{13}\text{O}_4$ , formed by the action of methyl iodide on the silver salt, crystallises in colourless needles, m. p. 124–125°, is hydrolysed by boiling alkalis, and when heated with hydrazine hydrate in methylalcoholic solution yields a *transformation product*, m. p. 174°, solidifying to a yellow substance, m. p. 150–151°.

The *bromophenylhydrazone*,  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_2\text{Br}$ , m. p. 221° (*loc. cit.*), has the constitution  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4(\text{OH})\cdot\text{CMe}(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})$ , and is a “transformation product” from which it is prepared, but of methyl resacetophenonecarboxylate; when heated with hydrogen chloride in glacial acetic acid at 125–130°, it yields a mixture of resacetophenonecarboxylic acid and its methyl ester.

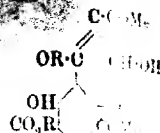
The “transformation products,” m. p. 162°, obtained by the action of magnesium methoxide on xanthophanic acid methyl and ethyl ethers respectively, are not identical, as they yield different bromides subsequent with hydrogen bromide in benzene solution. The *bromide*,  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{Br}$ , derived from the ethyl ester, crystallises in lemon yellow needles, m. p. 208° (decomp.), and when shaken with methyl or ethyl alcohol, acetone, or water is hydrolysed, yielding the “transformation product,”  $\text{C}_{15}\text{H}_{13}\text{O}_4$ . The *bromide*,  $\text{C}_{16}\text{H}_{15}\text{O}_4\text{Br}$ , derived from the methyl ester, crystallises in similar needles, m. p. 188° (decomp.), and hydrolysis yields the “transformation product,”  $\text{C}_{16}\text{H}_{15}\text{O}_4$ .

The constitution of these substances is discussed; it is concluded that the xanthophanic acid ethers have the structure I, and under the influence of magnesium methoxide are transformed into derivatives of the type II. In the transformation of the ethyl ether, a methyl is substituted for the carboxylic ethyl group. The hydroxyl substituent

tuted by bringing by the action of hydrazine sulphate is that of the heterocyclic nucleus:

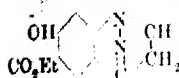


I.



II.

When boiled with hydrazine sulphate and sodium acetate in alcoholic solution, xanthophanic acid ethyl ether forms a *hydrazone* crystallising in needles, m. p. 193—195°, which is shown to have the annexed constitution, and is also formed also by the action of hydrazine on the ethyl ether.



The corresponding *hydrazone*,  $C_{11}H_{10}O_4N_2$ , derived from the ethyl ether, crystallises in needles, m. p. 220°. When heated with fuming hydrochloric acid or hydrogen iodide in acetic anhydride, or with alkali, these hydrazones yield the *acid*,  $C_{10}H_8O_4N_2$ , crystallising in yellowish-green needles, m. p. 331—333° (decomp.), and forming solutions with slight blue fluorescence.

**Glaucophanic Acid. III.** CARL LIEBERMANN and H. T. MANN (Ber., 1907, 40, 3584—3588. Compare Abstr., 1906, i, 270, and preceding abstract).—Glaucophanic acid methyl and ethyl ethers, which are formed as by-products in the preparation of xanthophanic acid methyl and ethyl ethers respectively, undergo reactions similar to those of the xanthophanic acid ethers, differing only in that the methyl and ethyl ethers yield identical magnesium acetate "transformation products." In the case of glaucophanic acid ethyl ether, therefore, the action of magnesium methoxide must lead to complete substitution of the ethoxy- by methoxy-groups, whereas the carboxylic ethoxy group of xanthophanic acid ethyl ether is substituted. The glaucophanic acid and xanthophanic acid ethers must have a  $C_{12}$  nucleus in common, as the action of hydrazine sulphate and sodium acetate on glaucophanic acid ethyl ether leads to formation of the *hydrazone*, m. p. 193—195°, obtained from xanthophanic acid ethyl ether.

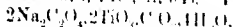
The magnesium methoxide "transformation product"  $C_{10}H_8O_6$  is formed from glaucophanic acid methyl ether in a 70% yield; it crystallises in yellow needles, m. p. 217°, and when heated with acetic anhydride and sodium acetate yields a *triacetate*,  $C_{10}H_8O_9Ac_3$ , which crystallises in needles, m. p. 130°, and is hydrolysed to the "transformation product" by cold concentrated sulphuric acid. In the presence of a limited amount of acetic anhydride, a yellow *diacetate*,  $C_{10}H_8O_7Ac_2$ , m. p. 166°, is formed. The *bromide*,  $C_{10}H_7O_6Br$ , crystallises in orange-red needles, m. p. 245°, and is stable when dry, but is readily hydrolysed by moist solvents. A *dibromide* compound,  $C_{10}H_6O_6Br_2$  or  $C_{10}H_5O_6Br_2$ , formed by the action of bromine on the

the formation of crystals in carbon disulphide solution, separates from ethyl acetate as crystals, m. p. 225° (decomp.).

The "transformation product" forms a hydrazone,  $C_{17}H_{17}O_2N_2$ , crystallising in white needles, m. p. 217° (decomp.), but when heated with bromophenylhydrazine in boiling methyl-alcoholic solution forms the bromophenylhydrazone of a decomposition product,  $C_{17}H_{17}O_2N_2Br$ , which crystallises in needles, m. p. 161–163° (decomp.), and resembles, but is not identical with, the bromophenylhydrazone obtained from the "transformation product" of xanthophanic acid methyl ether.

The molecular formula of glaucophanic acid ethyl ether, which remains unchanged, must lie between  $C_{13}$  and  $C_{27}$  (compare Claisen, Abstr., 1897, i, 304). G. Y.

**Certain Complex Salts of Titanium Peroxide.** ARRIGO, MARCHESINI (Atti R. Accad. Lincei, 1907, [v], 18, ii, 265–273, 342–343; compare this vol. i, 748; ii, 54). The compound,



prepared by adding excess of hydrogen peroxide to a solution of sodium titanio-oxalate and precipitated from solution by the addition of alcohol, is a dense, dark orange, sandy powder, which dissolves readily in water and is extremely hygroscopic in presence of alcohol. It remains unaltered for some time in a dry atmosphere, but in air it deliquesces, swells, and begins to decompose. The corresponding potassium compound,  $2K_2C_2O_4 \cdot 2TiO_2 \cdot C_2O_4 \cdot 2H_2O$ , prepared by adding alcoholic potassium acetate solution to alcoholic titanium hydrogen oxalate solution containing hydrogen peroxide, resembles the sodium derivative.

By adding an insufficient amount of barium chloride, together with ammonium acetate, to a solution of sodium titanio-oxalate containing the three constituents in the proportions  $TiO_2 : 2H_2C_2O_4 : 2Na$  and mixed with hydrogen peroxide, various fractions are precipitated which consist apparently of mixtures of  $2BaC_2O_4 \cdot 2TiO_2 \cdot C_2O_4$  and  $BaCO_3$ .

The complexity of the titanio-oxalates is shown by the ease with which they can be recrystallised, almost unchanged, from their solutions and by their resistance to hydrolysis by the action of heat. That the degree of complexity is not high is seen from the fact that the salts are decomposed, not only by alkalis, but even by an excess of sodium or calcium salt (compare Rosenheim and Schütte, Abstr., 1894, ii, 244). The alkali pertitanio-oxalates, however, are more highly complex, since they are not completely precipitated by ammonia. The fraction of active oxygen into the molecule of titanium oxide is, in general, favourable to the formation of complex anions. The statement of Melikoff and Pissarjewsky (Abstr., 1898, ii, 374) that, in the preparation of titanium peroxide, by Classen's method, each liquid at first contains an ammonium pertitanate, which becomes with precipitation of  $TiO_2 \cdot 4H_2O$ , is probably inaccurate; it is certainly that the  $TiO_2$  is present initially as a complex anion, which is gradually decomposed by the alkali.

The so-called acetate of titanium peroxide (Faber, this vol. ii, 557) is most probably a mixture of peroxide and basic acetate of titanium

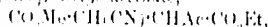
dioxide. The existence of the phosphate is in accord with  
of the author (*loc. cit.*). T. H. P.

**Velocity of the Decomposition of Malonic Acid into Carbon Dioxide and Acetic Acid.** JOSEF LINDNER (*Bull. Soc. chim.*, 1907, 28, 1041—1047).—The decomposition of malonic acid into carbon dioxide and acetic acid takes place with measurable velocity in glacial acetic acid at 100°. The velocity constant when compared with the aid of the equation for unimolecular reactions is satisfactorily uniform throughout the course of the decomposition. The graph formed by plotting the velocity constants determined at 98.5° to 104° against the temperatures is approximately a straight line.

**Action of  $\alpha$ -Chloroacetoacetic Esters on Sodicyanoacetate Esters.** J. CHASSAGNE (*Bull. Soc. chim.*, 1907, [iv], 1, 244—245). Compare: Haller and Bathe, *Abstr.*, 1888, 937).—Ethyl  $\alpha$ -chloroacetoacetate,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , prepared by the action of ethyl  $\alpha$ -chloroacetoacetate on ethyl sodicyanoacetate, separates from alcohol in crystals, m. p. 83.5—84.5 (corr.), and has a molecular weight in freezing acetic acid.

**Methyl  $\alpha$ -cyano- $\beta$ -acetylsuccinate**,  $\text{CO}_2\text{Me}\cdot\text{CH}(\text{CN})\cdot\text{CHAc}\cdot\text{CO}_2\text{Me}$ , similarly prepared, separates in crystals, m. p. 89.5—90.5.

**Methyl ethyl  $\alpha$ -cyano- $\beta$ -acetylsuccinate**,



obtained by the interaction of ethyl  $\alpha$ -chloroacetylacetate and ethyl sodicyanoacetate, forms crystals, m. p. 93.5—94.5. Ethyl  $\alpha$ -chloroacetoacetate,  $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$ , prepared from methyl  $\alpha$ -chloroacetylacetate and ethyl sodicyanoacetate, has m. p. 88.5—89.5.

Since these compounds in alcoholic solution give no reaction with ferric chloride, it is possible that they have an enolic structure.

T. H. P.

**Conversion of Methyl Alcohol into Formaldehyde. Preparation of Formalin.** E. J. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 855—868). Experiment shows that the ordinarily accepted method of the conversion of methyl alcohol into formaldehyde by means of ordinary method of preparation are essentially wrong. A special apparatus has been devised which yields satisfactory results for technical purposes. The first stage in the reaction is the catalytic decomposition of methyl alcohol, thus:  $\text{MeOH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$ . The catalysts employed were freshly reduced copper and asbestos, and precipitated lower oxides of vanadium. The former is the most efficient catalyst, but not more than 60% of the alcohol is actually changed. In addition, the formaldehyde decomposes, forming carbon monoxide and hydrogen, which together with carbon dioxide are generally found in the gaseous products. The presence of impurities such as acetone makes no difference in the decomposition of the alcohol.

L. K.

The Effect of Light and Temperature on the Preservation of Formaldehyde Solutions. J. W. de WAAL (*Pharm. Weekblad*, 1907, 44, 1207—1213).—At the ordinary temperature when exposed to light formaldehyde solutions are not oxidised to formic acid, even in presence of traces of ferric chloride. Rise of temperature promotes oxidation somewhat, although the effect produced by a temperature rise during 400 hours is only slight. A. J. W.

Synthesis of Ketones by aid of Dibromopentane. JULIUS VON LIESEN (*Ber.*, 1907, 40, 3943—3948. Compare Perkin and Freer, *ibid.*, 1888, 53, 202; Perkin and Kipping, *ibid.*, 1890, 57, 320).—Dibromopentane, ethyl acetacetate, and sodium react in warm alcoholic solution to form two compounds. *Ethyl 1-acetyl-4-cyclohexanecarboxylate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_{10}\cdot\text{COMe}$ , b. p. 241—245° (decomp.), or 10—11 mm., is a colourless liquid with a piercing aromatic odour, which forms a *semicarbazone*, m. p. 144°, and a *p-nitrophenyl-glydrazon*, m. p. 145°, and is hydrolysed by aqueous alcoholic alkali, giving *cyclohexanecarboxylic acid* and Darzens' and Bouveault's *cyclohexanyl ketone*, which has D<sub>20</sub> 0.893 and forms a reddish-brown *p-nitrophenylglydrazon*, m. p. 154°. The second compound is *ethyl 1-acetyl-4-cycloheptanecarboxylate*.

$\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ , b. p. 241—245° (decomp.), is very differently volatile with steam, and cannot be distilled and decomposes into the *diketone*,  $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ , the formation of which is completed by boiling with alkali. The diketone, m. p. 60°, crystallises in glistening leaflets, and forms a *semicarbazone*, D<sub>20</sub> 0.87, m. p. 184°, *p-nitrophenylglydrazon*,  $\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}_3$ , m. p. 88°, b. p. 85°, and an oxime which yields apparently a mixture of benzoyl derivatives, of which one has been isolated and has m. p. 100°. C. S.

Isolation of Carbohydrates and Glucosides by Precipitation with Metallic Salts. G. MILLURE (*J. Pharm. Chem.*, 1907, 26, 103—111). The method of precipitating carbohydrates and glucosides from the lead acetates under different conditions is discussed, and attention is drawn to various causes which tend to complicate the general precipitation. It is shown that copper acetate may be used in place of lead acetate for precipitating glucosides, the only precaution being that the precipitates are most readily formed in hot solutions. Fractional precipitation may be accomplished by working in the acid, neutral, and finally in ammoniacal solutions.

The copper method does not yield good results with many carbohydrates, especially lactose and maltose, as they reduce the copper salt. It may be employed for isolating inositol provided the liquid is saturated with ammonia. J. J. S.

Action of Cold Aqueous Sodium Hydroxide on Cellulose. WILHELM VIEWEG (*Ber.*, 1907, 40, 3876—3883).—Wichelhaus and Vieweg (this vol., i, 186) have shown that natural and mercerised celluloses differ from one another in chemical properties. The author shows the effect of the variation in strength of the sodium



hydride in cellulose. It has been shown that the amount of sodium hydroxide taken up by cellulose from alkaline solutions of varying concentration; the conclusion is drawn that a chemical reaction takes place. The compounds of sodium hydroxide and cellulose are completely decomposed by water, and a product remains which takes up more sodium hydroxide than the original cellulose. Samples of cellulose were found to differ with respect to the amount of sodium hydroxide which they take up; the "degree of mercerisation" varies from 1 to 3%, and may be estimated by the Schott-Baumann method.

**Chemistry and Physiological Action of the Humic Acids.** R. A. ROBERTSON, JAMES C. IRVINE, and MILDRED L. IRVINE (*Bio Chem J.*, 1907, 2, 458—480).—The natural humic acids prepared from peat differ greatly in composition, and also from the humic acids prepared from sucrose. The acids themselves and their salts serve as organic food for *Penicillium*, both as regards carbon and nitrogen.

**Further Observations on the Behaviour of Alkyl Attached to Nitrogen towards Boiling Hydriodic Acid.** G. GOLDSCHMIEDT (*Monatsh.*, 1907, 28, 1063—1068. Compare *ibid.*, 1904, 35, 1063; Goldschmidt and Hönigschmid, *Abstr.*, 1904, ii, 94).—When substances containing an alkyl group attached to nitrogen are boiled with hydriodic acid to yield the alkyl iodide, the reaction takes place to a greater or less extent depending on the structure of the nitrogenous compound. Negative results have been obtained previously with a number of compounds, including tetramethylammonium iodide, benzyltrimethylamine, and compounds such as betaine, sarcosine, and methylphenylphenone, containing the grouping  $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{NMe}$ , which in the pyridine series yields methyl iodide with special ease. The reaction towards boiling hydriodic acid of a number of compounds having the group  $\text{N}\cdot\text{Alkyl}$  attached to a tertiary aliphatic carbon has not been investigated, as such substances resemble aromatic amines in certain respects.

When boiled with hydriodic acid, b. p. 127°, for six hours, and then for a further six hours with hydriodic acid, D 1.9, the following substances yield the percentages quoted of the  $\text{N}\cdot\text{Alkyl}$  group as alkyl iodide: 1:2:4:4-tetramethyltrimethylenimine, 5.4%; 2:2:4:4-tetramethyl-1-ethyl-trimethylenimine, 2.5%; methylidiacetonealkamine, 10.7%; methylpropyldiacetonealkamine, 20.5%;  $\beta$ -dimethylacetonealkamine, 14.1%;  $\Delta^1$ -pentene, 1.4%. On the other hand,  $\alpha$ -methylamino- $\beta$ -methylphenol, in which the methylamino-group is attached to a tertiary carbon atom, does not yield methyl iodide. Since the propyl group must be less reactive than the ethyl group, the high percentage obtained with methylpropyldiacetonealkamine cannot be ascribed to the formation of propyl iodide.

Whilst the average stability of the methyl group in  $\beta$ -dimethylacetonealkamine is greater than the stability of the methyl group in  $\alpha$ -methylamino- $\beta$ -methylphenol, the average stability of the methyls of a trimethylammonium iodide is much smaller, and the velocity of the reaction

d methyl iodide is 100% greater. Tetramethylammonium iodide and a half hour yields 0.4%, dimethylaniline is eleven and a half hours, 3.9%, and phenyltrimethylammonium iodide in two hours 1.5% of the total methyl as methyl iodide. Of interest as compared with the behaviour of dimethylaniline is that of tetramethylbenzylidene which in eleven and a half hours yields 7.02% of its methyl as methyl iodide.

When boiled with hydriodic acid, *o*-phenylmethylhydrazine yields 23% of the methyl as methyl iodide; at the same time, free iodine formation in consequence of the reduction of the hydrazine. Which of these is the primary reaction cannot be decided.

**Bis-aquo-chromium Salts.** PAUL PFEIFFER (and, in part, ARMIN MACHOWAN, STERN, and PRADE) (*Ber.*, 1907, 40, 3828-3839).—A series of salts of the diethylenediaminechromium series have been prepared corresponding with the recently described diaquotetraamminechromium salts (Pfeiffer, this vol., ii, 694). In each case, however, it was found that the diethylenediamine salt contains twice the amount of water not removed in a desiccator which is present in the corresponding diethylenediamine compound; consequently it is necessary to assume that the single water molecules in the metal complex of diamine salts are replaced by  $O_2H_2$  molecules in the diethylenediamine compound. The author proposes to name such salts containing the  $O_2H_2$  complex, *bis-aquo*-salts (compare Werner and Tubber, *ibid.*, 1906, ii, 452).

23. *Ph. edisiquo-liethylenedianinechromium bromide.*

originally wrongly described as a monoquo-salt (Abstr., 1905, 54). A concentrated solution of the salt yields with potassium cyanide, a brilliant, crystalline, red powder; with potassium cyanate, the orange *cis*-dithiocyanato(dithylenedi-imino)chromium thio-donate,  $[\text{Cr}(\text{CSN})_2]\text{SCN}$ ; with ammonium oxalate, the bordeaux-donate salt,  $[\text{Cr}(\text{C}_2\text{O}_4)_2][\text{Cr}(\text{C}_2\text{O}_4)_2]$ ; with potassium chromi-cyanate, the *heazthochromic* salt.

calcing in brilliant, violet-red, transparent needles, which are soluble in light. Concentrated nitric acid probably converts the nitrate; obtained as an orange red precipitate.

[En<sub>2</sub>Cr(O<sub>2</sub>H<sub>3</sub>)OH]Br<sub>3</sub>

ated by the action of pyridine on the bromobis(aquo-bromide, red complex), bordeaux-red crystals. A concentrated solution of the reaction with silver nitrate a precipitate of silver bromide free from triethylamine; with potassium iodide, a red, crystalline precipitate of the iodide. Concentrated hydrobromic acid converts the salt *triethylammoniumdiethylenediaminechromium bromide*.

$[\text{Eu}(\text{Cr}(\text{O}_2\text{H})_2)_2]\text{Br}_3$ . This salt is obtained by pyridine into the hydroxybisaquo-bromide and slowly by bromous acid at the ordinary temperature into the bromobisaquo-bromide. A concentrated aqueous solution of the salt yields with

solid potassium oxalate, small, brilliant, orange leaflets of. The salt is converted when heated alone at 100—120° evaporated with hydrobromic acid on a water-bath, into the form of *cis*-dibromodiethylenediaminechromium bromide. This substance is also obtained, by evaporating a solution of bromobis-aquo bromide with a drop of hydrobromic acid on a water-bath, in the form of a violet powder. The anhydrous salt is obtained by small quantities of water into a *monohydrate*: obtained as a crystalline, violet powder. The *iodide* forms glittering, the *dithionate* forms brilliant bluish-violet needles; obtained as a violet powder.

**Complex Derivatives of Optically Active Propylenediamine.** LEO ISCHIGALEFF and W. SOKOLOFF (*Ber.*, 1917, 3461—3465).—The great increase in optical activity of *l*-propylenediamine, on the addition of certain salts to various optically-active compounds containing hydroxy-groups, has been ascribed by Walden to the formation of cyclic complexes. The influence of ring formation on optical rotation has been investigated by the authors with a series of derivatives of *l*-propylenediamine, the cyclic nature of the derivatives of *dl*-propylenediamine having already been shown by Werner.

*l*-Propylenediamine, obtained by the resolution of the *dl*-tartaric acid, has  $[\alpha]_D^{25}$  121°,  $D_4$  0.8633,  $[\alpha]_D^{25}$  +28.4°. Baumann gives  $D_4^{25}$  0.91186 and  $[\alpha]_D^{25}$  +20.96°.

*l*-Propylenediamine hydrochloride,  $C_3H_9(NH_2)_2 \cdot 2HCl$ , has  $[\alpha]_D^{25}$  1.0575, and  $[\alpha]_D^{25}$  +4.01 (in aqueous solution,  $p$  1.010).

The platinum compounds studied were prepared by the action of platinum *cis*-dichloro *l*-propylenediamine,  $[Pt(Pn)_2Cl_2]$ , on a solution at 100° and the calculated amount of the organic bases (*l*-propylenediamine, ammonia, ethylenediamine, or triethylenediamine); the resulting solutions were concentrated and the compounds precipitated by the addition of alcohol or a mixture of alcohol and alcohol.

The compound,  $[Pt(Pn)_2Cl_2]$  (where  $Pn = NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ ), has  $[\alpha]_D^{25}$  +46.37 for  $p$  1.661 and  $D_4$  1.0958. [Solvent,  $CH_2Cl_2$ ; this and other cases. (Abstractor.)]

The compound,  $[Pt(Pn)_2Cl_2]$ , has  $[\alpha]_D^{25}$  +25.17 for  $p$  1.661 and  $D_4$  1.1111.

The compound,  $[Pt(Pn)_2Cl_2]$ , has  $[\alpha]_D^{25}$  +21.07 for  $p$  1.661 and  $D_4$  1.1135.

The compound,  $[Pt(Pn)_2Cl_2]$ , has  $[\alpha]_D^{25}$  +23.04 for  $p$  1.661 and  $D_4$  1.0747.

The compound,  $[Pt(Pn)_2Cl_2]$ , obtained from  $K_2PtCl_6$  and *l*-propylenediamine, has  $[\alpha]_D^{25}$  +76.25 for  $p$  1.768 and  $D_4$  1.1771.

The compound,  $[Pt(Pn)_2Cl_2 \cdot 2H_2O]$ , has  $[\alpha]_D^{25}$  +11.41 for  $p$  1.010 and  $D_4$  1.0253.

It will be observed that, although *l*-propylenediamine is optically

these are investigatory, the metallic derivatives examined are preparatory.

The influence of the number of propylenediamine molecules in the complex molecule of the platinum derivatives is clearly seen by a comparison of the molecular rotations of these compounds. A. McK.

**Isomeric  $\alpha\beta$ -Dialkylhydroxylamines.** I.  $\alpha$  Methyl- $\beta$ -ethylhydroxylamine. II.  $\beta$ -Methyl- $\alpha$ -ethylhydroxylamine. LAUDER W. JONES, *Amer. Chem. J.*, 1907, 33, 253—257. It has been shown previously (Abstr., 1898, i, 174) that when the sodium salt of hydroxyurethane (carboethoxyhydroxamic acid) is treated with methyl iodide, the methyl ether,  $\text{OEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{OMe}$ , is produced together with  $\alpha$ -methylcarboethoxyhydroxylamine (hydroxymethylmethane methyl ether),  $\text{CO} \cdot \text{Et} \cdot \text{NH} \cdot \text{Me} \cdot \text{OMe}$ , which on hydrolysis yields  $\beta$ -methylhydroxylamine. The corresponding ethyl derivatives were obtained in a similar manner.

When hydroxyurethane methyl ether is treated with ethyl iodide a mixture of sodium ethoxide, *carboethoxy- $\alpha$ -methyl- $\beta$ -ethylhydroxylamine- $\beta$ -hydroxyurethane methyl ether*,  $\text{CO} \cdot \text{Et} \cdot \text{NEt} \cdot \text{OMe}$ , b. p. 166—167°, is produced as a colourless oil which has a peculiar, rather unpleasant odour. If this compound is heated with strong hydrochloric acid it is converted into a methyl- $\beta$ -ethylhydroxylamine,  $\text{NHMe} \cdot \text{OEt}$ , d. 0.86—0.91, which is a colourless, alkaline liquid, readily soluble in water and does not reduce silver nitrate; the hydrochloride, m. p. 174 (approx.), and the *platinichloride*, m. p. 174—175° (decomp.), are formed.

Similarly, methyl iodide reacts with hydroxyurethane ethyl ether to form *carboethoxy- $\beta$ -methyl- $\alpha$ -ethylhydroxylamine- $\beta$ -hydroxymethylmethane-ethyl ether*,  $\text{CO} \cdot \text{Et} \cdot \text{NMe} \cdot \text{OEt}$ , b. p. 166—167°, which on hydrolysis yields  $\beta$ -methyl- $\alpha$ -ethylhydroxylamine,  $\text{NHMe} \cdot \text{OEt}$ , b. p. 166—167°, which furnishes a *hydrochloride*, m. p. 74—75°, and a *platinichloride*, m. p. 170—171° (decomp.). E. G.

**Preparation of Acylated Aminoalkyl Esters.** J. D. RIEDEL, U. S. P. 1,1175. Compare Abstr., 1906, i, 631). This patent covers the preparation of substances having the general formula  $\text{R}^1 \cdot \text{R}^2 \cdot \text{H}_2 \cdot \text{CR}^3 \cdot \text{R}^4 \cdot \text{OR}$ , where R and  $\text{R}^3$  are acyl groups and  $\text{R}^1$  and  $\text{R}^2$  are alkyl, aryl, or mixed arylalkyl groups. These compounds have useful antipyretic and hypnotic properties.

*Chlorodimethylthylethylcarbinol*,  $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CMeEt} \cdot \text{OH}$ , an oil, b. p. 52—53 mm., was obtained by heating chlorodimethylthylethylcarbinol with ammonia in 25% alcoholic solution.

*Chlorodimethylthylethylcarbinol valerate*,

$\text{NHMe} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CMeEt} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , b. p. 45—46 mm., was prepared by the action of valeryl chloride and sodium hydroxide on the preceding compound.

*Chlorophenylthymethylthylethylcarbinol*,  $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CMePh} \cdot \text{OH}$ , b. p. 47—48 mm., obtained from chlorophenylthymethylthylethylcarbinol and ammonia on treatment with benzoyl chloride at 150°, yielded *phenylthymethylthylethylthymethylthylethylcarbinol benzoate*,

$\text{NMeEt} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{Ph} \cdot \text{O} \cdot \text{OBz}$ .

G. T. M.

**Hydroxy and Amino Compounds.** *Normal Primary Butylamine.*  $\text{C}_4\text{H}_{11}\text{N}$ . *B. p.* 126° (33–327). — ***3-Ethoxybutylamine.***  $\text{C}_6\text{H}_{15}\text{NO}$ .  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ . *b. p.* 133–154°/746 mm.,  $D_4^{20}$  0.8640,  $n_D^{20}$  1.42751, obtained by refluxing 3-ethoxybutyronitrile by Ladenburg's method, is a colourless, mobile liquid of disagreeable odour and piquant taste, and dissolves in water with development of heat, probably forming a hydrate.

**Aminoethyl ether**,  $\text{NH}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{OEt}$ , boils at 73° higher than ethyl ether and 89° higher than ethylamine, whilst ***3-ethoxybutylamine*** boils only 62° higher than ethyl butyl ether and 78° higher than normal primary butylamine, so that the influence on volatility of the two components,  $-\text{CH}_2 \cdot \text{NH}_2$  and  $-\text{CH}_2 \cdot \text{OEt}$ , is less marked when they are separated by the system  $-\text{CH}_2 \cdot \text{CH}_2 \cdot$  than when they are close together.

The fall in boiling point due to the conversion of normal primary butyl alcohol into the corresponding ethyl ether is 25°, and the resulting from the change of  $\delta$ -hydroxybutylamine into *3-ethoxybutylamine* is 53°. Similarly, the increase in boiling point due to the introduction of the  $\text{NH}_2$  group into normal butane is 74°, whilst that due to the introduction of the same group in the  $\delta$ -position in normal butyl alcohol is 90°. These differences are probably due to the interaction between the  $-\text{CH}_2 \cdot \text{OH}$  and  $-\text{CH}_2 \cdot \text{NH}_2$  groups being greater than that between the groups  $-\text{CH}_2 \cdot \text{OEt}$  and  $-\text{CH}_2 \cdot \text{NH}_2$ .

The increase of boiling point resulting from the conversion of normal paraffins into the corresponding primary alcohols is greater than that due to their conversion into the corresponding primary amines, probably because the alcohols are associated. Similarly, the increase in boiling point on passing from alcohols to their corresponding glycols is greater than that observed in changing from monoamines to the corresponding diamines.

The transformation of an amine into the corresponding amino alcohol is accompanied by a rise of boiling point almost as great as that observed on passing from the hydrocarbon to the corresponding alcohol, and is greater than that due to the conversion of the alcohol into the corresponding amino alcohol, as the following example shows:  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{NH}_2 \rightarrow \text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ ,  $+152^\circ$ ;  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ ,  $+93^\circ$ . This difference is probably due, in part, to the action of the  $-\text{CH}_2 \cdot \text{NH}_2$  and  $-\text{CH}_2 \cdot \text{OH}$  groups.

The increase in boiling point resulting from the change from the simple alcohol to the glycol or from the monoamine to the diamine is less than that due to the conversion of the hydrocarbon into the simple alcohol or monoamine respectively, and as the difference between the increases due to the two changes, hydrocarbon  $\rightarrow$  alcohol  $\rightarrow$  glycol, is greater than that exhibited in the case of the two changes, hydrocarbon  $\rightarrow$  monoamine  $\rightarrow$  diamine, it may be assumed that the mutual action between two  $-\text{CH}_2 \cdot \text{OH}$  groups is greater than that between two  $-\text{CH}_2 \cdot \text{NH}_2$  groups. This also explains the fact that a greater difference in volatility is shown between successive members in a homologous series of diamines than between successive members of a homologous series of glycols. The differences observed in the

lower boiling homologous alcohols. The replacement of an  $\text{OH}$  group in a given alcohol by an  $\text{NH}_2$  group gives rise at the same  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  to the same lowering (24–26°) of the boiling point, and this value is less than that (41–59°) due to the replacement of  $\text{OH}$  in a simple alcohol by  $\text{NH}_2$ . The former case affords a further example of the mutual influence exerted by the groupings  $-\text{CH}_2\text{NH}_2$  and  $-\text{CH}_2\text{OH}$ .

T. A. R.

**Diacetoneamine.** MORITZ KOHN (*Monatsh.*, 1907, 38, 1049–1056).—It has been shown previously that the action of magnesium methyl iodide on diacetone alcohol leads to the formation of  $\beta$ , $\beta$ -dimethylpentane- $\beta$ , $\delta$ -diol (Franke and Kohn, *Abstr.*, 1905, i, 111, this vol., 171). The action of magnesium methyl iodide on diacetoneamine is found now to lead in the same manner to the formation of  $\beta$ -amino- $\beta$ , $\beta$ -dimethylpentane- $\delta$ -ol, only a small amount of the diacetoneamine undergoing decomposition into ammonia and mesityl oxide.

$\beta$ -Amino- $\beta$ , $\beta$ -dimethylpentane- $\delta$ -ol,  $\text{NH}_2\text{CMe}_2\text{CH}_2\text{CMe}_2\text{OH}$ , is obtained as a mobile oil, b. p. 82/19–20 mm., has a slight ammoniacal odour, and absorbs carbon dioxide rapidly on exposure to air. The *platinichloride*,  $(\text{C}_{11}\text{H}_{21}\text{ON})_2\text{H}_2\text{PtCl}_6$ , crystallises in scarlet rhombohedral plates; the *picrate*,  $\text{C}_{13}\text{H}_{20}\text{ON}, \text{H}_2\text{AuCl}_6$ , forms monoclinic crystals, m. p. 153–155.5°; the *osadate*, m. p. 212° (decomp.). The action of methyl iodide on  $\beta$ -amino- $\beta$ , $\beta$ -dimethylpentane- $\delta$ -ol leads to the formation of a base which yields an *aurochloride*,  $\text{C}_{10}\text{H}_{19}\text{ON}, \text{HAuCl}_4$ , crystallising in golden leaflets, m. p. 142–143°.  $\beta$ -Phenylthio- $\beta$ -amino- $\beta$ , $\beta$ -dimethylpentane- $\delta$ -ol,  $\text{C}_{11}\text{H}_{21}\text{ON}, \text{S}$ , formed by the action of phenylthiocarbimide on  $\beta$ -amino- $\beta$ , $\beta$ -dimethylpentane- $\delta$ -ol, crystallises in white leaflets, m. p. 115–117°.

G. Y.

**Cyanogen Bromide as a Means of Testing the Stability of Groups attached to Nitrogen.** JULIUS VON BRAUN (*Ber.*, 1907, 40, 3933–3943).—Previous investigations (*Abstr.*, 1900, i, 59, 641, 687; 1902, i, 365; 1903, i, 464) have shown that the action between tertiary bases and cyanogen bromide is represented by  $\text{N}^{\text{R}^1}\text{R}^2 + \text{BrCN} = \text{NR}^1\text{R}^2\text{CN} + \text{R}^2\text{Br}$ , and that the series allyl, vinyl, methyl, ethyl, propyl, isopropyl, and phenyl denotes the increasing difficulty with which the group  $\text{R}^2$  is eliminated. Tertiary bases containing the group  $-\text{CH}_2\text{CN}$  or  $-\text{CH}_2\text{CO}_2\text{Et}$  ( $=\text{X}$ ) react as  $\text{NRX} + \text{BrCN} \rightarrow$  (I)  $\text{NR}_2\text{CN} + \text{BrX}$  or (II)  $\text{NRX-CN} + \text{Br}$ . Reaction (I) increases and (II) diminishes as R increases from methyl to butyl.

*Isopropylpiperidinium bromide*,  $\text{C}_5\text{NH}_{10}(\text{CH}_2\text{CN})_2\text{Br}$ , obtained from isopropylammoniumacetonitrile and bromoacetonitrile, has m. p. 173° (decomp.). The *platinichloride*, m. p. 192° (decomp.), forms reddish-brown crystals.

Dimethylaminoacetonitrile and cyanogen bromide react energetically to form *cyanomethylaminoacetonitrile*,  $\text{CN}\cdot\text{NMe}\cdot\text{CH}_2\text{CN}$ , b. p. 40–45/12 mm., and methyl bromide; the latter reacts with the unchanged dimethylaminoacetonitrile to form *trimethylcyanomethylammonium bromide*,  $\text{CN}\cdot\text{CH}_3\cdot\text{NMe}_3\text{Br}$ , which is readily converted into

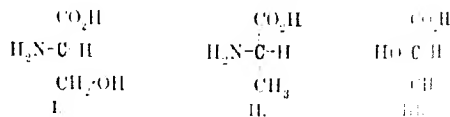
betaine. The odour of bromoacetonitrile is perceptible only when large quantities of dimethylaminoacetonitrile and cyanogen bromide are reacting.

Diethylaminoacetonitrile and cyanogen bromide react to form diethylethylaminoacetamide, bromoacetonitrile, *cycloethylaminoacetamide*,  $\text{CN}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 150–9 mm., and *ethylaminoacetamide*,  $\text{NH}_2\text{Et}\cdot\text{CH}_2\cdot\text{CN}$ , HBr. Ethyl diethylglycine and cyanogen bromide yield diethylethylaminoacetamide, ethyl bromoacetate, and *ethyl diethylglycine*,  $\text{CN}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 139°.

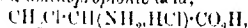
*Dipropylaminoacetonitrile*,  $\text{NPr}_2\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 89–90 mm., is obtained from dipropylamine by Knoevenagel's method (Ann., 1904, i, 981); the *methiodide* sinters at 130° and has m. p. 135° (decomp.). It reacts with cyanogen bromide at 100° to yield dipropylethylaminoacetamide, bromoacetonitrile, and 20–25% of *propylethylaminoacetonitrile*,  $\text{CN}\cdot\text{NPr}\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 155–156°/12 mm.

*Ethyl dipropylglycine*,  $\text{NPr}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained from dipropylamine and ethyl bromoacetate, has b. p. 204° (decomp.) or 174°/12 mm., and reacts with cyanogen bromide to form probably *ethyl propylethylaminoacetamide*, dipropylethylaminoacetamide, and ethyl propylethylaminoacetamide. *Diisobutylaminoacetonitrile*,  $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CH}_2\cdot\text{CN}$ , b. p. 95–96 mm., requires heating for thirty hours with cyanogen bromide; the products have not been definitely isolated. *Diisobutylaminoacetonitrile*,  $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CHMe}\cdot\text{CN}$ , b. p. 101–102°/10 mm., reacts with cyanogen bromide,  $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CHMe}\cdot\text{CN}$ , b. p. 129–132 mm., reacts less favourably with cyanogen bromide.

**Conversion of *L*-Serine into *D*-Alanine.** EMM. FISHER AND KARL RASKE (*Ann.*, 1907, 40, 3717–3724).—The conversion of *L*-serine into *D*-alanine is effected by treating the hydrochloride of *L*-serine methyl ester with acetyl chloride and phosphorus pentachloride, whereby the *hydrochloride* of *methyl 1-β-chloro-α-aminopropionate*, m. p. 157° (decomp.), is obtained (Fisher and Jacobs, this vol., 884, 885). By hydrolysis with 20% hydrochloric acid at 100° yields the *hydrochloride* of *1-β-chloro-α-aminopropionic acid*; the free acid, obtained by lithium or ammonium hydroxide, is reduced to *D*-alanine by zinc amalgam in faintly acid solution. It is highly probable that the reactions are optically normal, and therefore the known optical activity of *L*-serine (I) determines that of *D*-alanine (II) and also of *D*-alanine acid (III) obtained from the latter by the action of nitrous acid.



The following constants are given. In aqueous solution the *hydrochloride* of 1-β-chloro-α-aminopropionic acid,



has  $[\alpha]_D^{20} + 0.7^\circ$ , and the acid itself,  $[\alpha]_D^{20} - 15.16^\circ$ . *γ*-β-chloro-α-aminopropionic acid, m. p. 160° (decomp.), is reduced to *D*-alanine by zinc

*amino acid*  $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CO}_2\text{H}$  (m. p. 172° (decomp.)), crystallises in slender needles, and is converted by ammonium hydroxide at 100° into Kleb's hydrochloride of *α*-dimethylpropionic acid. The hydrochloride of methyl *β*-chloro-*α*-amino-propionic acid has m. p. 134° (decomp.).

C. S.

**Aminotrimethylacetic [ $\beta$ -Amino- $\alpha\alpha$ -dimethylpropionic] Acid.** M. BLAISE and AUGUST SCHMIDT (*Monatsh.*, 1907, 28, 1055—1062).

Four of the twelve possible aminovaleric acids have been prepared by Schmidt (Abstr., 1902, i, 206). A fifth isomeride is described in the present paper.

*β*-Amino- $\alpha\alpha$ -dimethylpropionic acid, m. p. 47° (40.5—41°; Blaise and Maréchal Abstr., 1904, i, 283), is obtained in a 65—70% yield by treating hydroxypivalic acid at 80° and then at 100° with aqueous hydrogen bromide saturated at 0°. *β*-*Isoto*- $\alpha\alpha$ -dimethylpropionic acid,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , prepared by boiling hydroxypivalic acid with hydrosulphuric acid, D 1.7, and amorphous phosphorus in a reflux apparatus, crystallises in glistening prisms, m. p. 51°.

*β*-Amino- $\alpha$ -dimethylpropionic acid,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}(\text{Me})_2\cdot\text{CO}_2\text{H}$ , obtained in 50% yield by the action of alcoholic ammonia, saturated at 0°, on *isoto*- $\alpha\alpha$ -dimethylpropionic acid at the ordinary temperature, crystallises in needles, decomp. about 220°, and forms a copper salt crystallising in microscopic, hexagonal plates. The benzoyl derivative,  $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}(\text{Me})_2\cdot\text{CO}_2\text{H}$ , crystallises in thin needles, m. p. 149—151°. The benzoyl ester derivative,  $\text{C}_{12}\text{H}_{19}\text{O}_5\text{N}$ , crystallises in needles, m. p. 72—73°. The methylated base forms a hydrochloride as a white, granular mass; the aurichloride,  $\text{C}_{12}\text{H}_{19}\text{O}_5\text{N}, \text{HAuCl}_4$ , crystallises in needles, m. p. 195—201° (decomp.); the picrate crystallises in plates, m. p. 224—225° (decomp.).

G. Y.

**Polypeptides. XXI. Derivatives of Tyrosine and of glutamic Acid.** EMIL FISCHER (*Ber.*, 1907, 40, 3704—3717, compare this vol., i, 652, 681, 737).—*d*-Alanyl-glycyl-*L*-tyrosine and *ε*-carboxyglycyl-*L*-tyrosine have been examined in anticipation of the study of the complex derivatives of tyrosine obtained, among other things, by the partial hydrolysis of silk fibroin. *d*- $\alpha$ -Bromoglycyl-*L*-tyrosine,

$\text{CH}_3\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 157—158°, obtained by the interaction of glycyl-*L*-tyrosine and *α*-bromopropionyl chloride in cold alkaline solution, separates from benzene-gated beulets, and has in aqueous solution  $[\alpha]_D^{20} + 50.6^\circ$ . Treatment with 25% ammonium hydroxide for three and a half hours at 25° it is converted into *d*-alanylglycyl-*L*-tyrosine,

$\text{NH}_2\cdot\text{CH}(\text{Me})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 149° and darkens at 180°; responds to Millon's and ninhydrin reactions, and has  $[\alpha]_D^{20} + 41.9^\circ$  in aqueous solution. *ε*-Carboxy-*ε*-carboxyglycyl-*L*-tyrosine,

$\text{CH}_3\cdot\text{CH}(\text{Br})\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_3\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , prepared from *L*-tyrosine and *d*- $\alpha$ -bromoisohexoyldiglycylglycyl chloride in cold alkaline solution; it crystallises in needles, and has  $[\alpha]_D^{20} + 28.7^\circ$  in aqueous solution. The air-dried substance softens at 100°. ACH. i.



100°, and has m. p. 115° (decomp.) whilst the anhydrous compound softens at 100°, gradually darkens, and has m. p. 220°. Methyl triglycyl-L-tyrosine,  $C_{21}H_{31}O_7N_5$ , obtained from the preceding and 25% ammonium hydroxide at 25°, is a colourless, crystalline substance, which begins to decompose at 160°, and has  $[\alpha]_D^{20}$  in aqueous solution. It has a bitter taste and an acid reaction, and is precipitated by Millon's and the biuret tests, and forms an amorphous picrate, and picrolonate, and a dark blue copper salt. The optical activity of this pentapeptide and of the preceding tripeptide is characterized by being precipitated from aqueous solution by ammonium sulphate, a behaviour which recalls that of the albumoses and also of the tripeptide obtained by Fischer and Abderhalden (this vol. 11, 117) and the partial hydrolysis of silk fibroin.

Glutamic acid is contained in many proteins, but the synthesis of polypeptides has hitherto been retarded by the difficulty of obtaining crystalline derivatives of the acid. *L-Leucyl-L-glutamic acid*,  $C_{14}H_{25}NO_7$ , m. p. 232° (decomp. corr.), obtained by the action of 25% ammonium hydroxide on *D*- $\alpha$ -bromoisohexoyl *D*-glutamic acid, soluble in water in long needles, has  $[\alpha]_D^{20} + 10.5^\circ$  in *N*-hydrochloric acid, and is precipitated from a solution in dilute sulphuric acid by platinum chloride, and forms easily soluble sodium and barium salts. On the other hand, the silver salt is sparingly soluble in water; in view of this property, many derivatives of glutamic and also of aspartic acid can be separated from other polypeptides.

The *D*- $\alpha$ -bromoisohexoyl *D*-glutamic acid, m. p. 108°, which is required in the preceding preparation, is prepared from *D*-glutamic acid and *D*- $\alpha$ -bromoisohexoyl chloride in cold alkaline solution. *Triglycylglycinamide*,  $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$ , is prepared by heating methyl triglycylglycine for two hours at 80–100° with methyl alcoholic ammonia saturated with ammonia; it crystallises in slender needles, sinters and darkens at 120°, and a solution in the dilute acid yields the nitrate and the hydrochloride. The picrate forms orange-red leaflets, and has m. p. 240°. Methyl pentaglycylglycine is converted only partially into the acid by liquid ammonia at the ordinary temperature, or by methylamine in alcoholic ammonia at 100°.

The molecular weights of glycyl-L-tyrosine, diglycyl-L-tyrosine, glycylglycine, leucylglycylglycine, *D*-alanylglycylglycine, *D*-phenylglycylglycine, and glycyl-L-valine anhydride, determined in aqueous solution by the cryoscopic method, are approximately normal. The acylation of tyrosine leads, as a rule, to the formation of *ortho*-derivatives; formic acid, however, yields *formyl-L-tyrosine*,  $OH \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CH(OH) \cdot CO_2H$ , which has m. p. 171–174° (decomp. corr.) in the anhydrous form, and  $[\alpha]_D^{20} + 84.9^\circ$  in alcoholic solution.

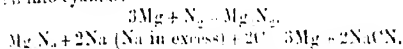
**Preparation of Alkyl Dialkylmalonamates.** *ALKYL-11*  
FABRIK AUF ARTEN (VORM. E. SCHERING) (D.R.-P. 182,477) *ALKYL-12*  
dialkylmalonamates are employed in the production of the *ALKYL-13*

barbituric acids. *Ethyl diethylmalonamate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{OEt}\cdot\text{CO}\cdot\text{Et}$ , m. p.  $79^\circ$ , is preferably produced by alkylating ethyl malonamate in two stages by the repeated action of ethyl iodide in sodium ethoxide.

*Ethyl dipropylmalonamate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{OPr}\cdot\text{CO}\cdot\text{Et}$ , white needles, m. p.  $12^\circ$ , is prepared by the action of sodium (2 atoms) and propyl iodide (2 mols.) on ethyl malonamate in alcoholic solution.

The alkyl sulphates may also be employed in producing the alkyl malonamates. G. T. M.

**Production of Alkali Cyanides.** Otto Schmir (D.R.P. 251,315). Compare this vol. i, 293. By passing nitrogen over a mixture of magnesium, carbon, and an alkali carbonate, an amount of alkali cyanide is obtained equivalent to the quantity of the magnesium present. If, however, the carbonate is replaced by the alkali metal itself, it becomes possible to convert a much larger proportion of the metal into cyanide.



One molecule of magnesium will bring about the transformation of 6 molecules of sodium into sodium cyanide. The magnesium has apparently a specific action on the absorption of nitrogen, and the formation of sodium cyanide occurs far more rapidly and completely in the absence of this metal. G. T. M.

**Glutamine.** ERNST SCHULZE and CH. GOBLI (*Landw. Versuchs-Stat.*, 1907, 33, 319). Compare this vol. i, 144. Fresh preparations of glutamine from (1) sugar-beet and (2 and 3) mangolds gave +16%, +8%, and +9.5% respectively. At  $16^\circ$ , it dissolves in 25.7 parts of water; the copper derivative,  $\text{Cu}(\text{C}_5\text{H}_9\text{O}_2\text{N})_2$ , can be obtained as rather lustrous violet crystals by heating a solution of glutamine with cuprous acetate. The calcium derivative,  $\text{Ca}(\text{C}_5\text{H}_9\text{O}_2\text{N})_2$ , obtained by precipitating the precipitated calcium hydroxide to a heated solution of glutamine until no longer dissolved, separates in fine prisms; when boiled with water, the compound is slowly hydrolysed.

Glutamine (1 mol.) forms a compound with tartaric acid (1 mol.) which separates in rather large, transparent crystals. N. H. J. M.

**Calcium Cyanamide. II.** GEORG BRÜNG, W. FRAENKEL, and WILHELM ZIEGLER (*Zeitsch. Elektrochem.*, 1907, 13, 605-612). Compare this vol. i, 145. The influence exerted by various substances on the absorption of nitrogen by calcium carbide has been further studied. Experiments with glaucum, magnesium, and strontium chlorides confirm the view that for metals in the same periodic group the velocity of the reaction is greater the lower the atomic weight of the metal. This relationship holds for 10% admixture. The formation of cyanide increases, on the other hand, with the atomic weight of the metal; the quantity is always small. Metallic calcium, magnesium, and sodium do not appreciably accelerate the absorption of nitrogen compared with the carbide. The view that the nitrogen absorption is partly due to calcium produced from the carbide is not supported.

by these experiments. The acceleration of the reaction, either alone or mixed with other substances, may be connected with the rate of the reaction. The authors suppose that the acceleration phenomena are connected with the fusibility of the added substance and the solubility of the carbide in the flux. For each flux, however, there may be a specific reaction constant. Determination of the velocity of the nitrogen absorption in nitrogen at different pressures shows that it is proportional to the pressure of the gas. Whether the acceleration is due to absorption, or chemical reaction is the determining factor. The velocity of the reaction has not yet been ascertained. H. N. S.

**Compounds of Ethylcarbylamine with Cobaltous, Ferrous and Ferric Chlorides.** KARL A. HOFMANN and GEN. A. DEZAR (Ber., 1907, 40, 3759—3761. Compare this vol., i, 419; R. 1907, 36, 604).—Guilleminard, in another way (this vol., i, 300), has arrived at the authors' conclusion that metallic cyanides are of the  $\text{M}(\text{CN})_3$  type.

*Cobaltous chloride bisethylcarbylamine*,  $\text{CoCl}_2 \cdot 2\text{EtNC}$ , obtained from its constituents in methyl-alcoholic solution, forms golden-yellow crystals; the chlorine is precipitated completely by silver nitrate. *Ferrous chloride bisethylcarbylamine*,  $\text{FeCl}_2 \cdot 2\text{EtNC}$ , similarly obtained in ethereal solution, forms stout, yellow prisms. *Ferric chloride triphenylcarbylamine*,  $\text{FeCl}_3 \cdot 3\text{PhNC}$ , crystallises in golden-yellow plates. *Ferric oxychloride tetra-ethylcarbylamine*,  $\text{FeOCl}_2 \cdot 4\text{EtNC}$ , obtained from ferrous chloride and ethylcarbylamine in ethereal solution, forms yellow plates. *Ferric oxychloride penta-ethylcarbylamine*,  $\text{FeOCl}_2 \cdot 5\text{EtNC}$ ,

is obtained in golden-yellow crystals from a 6% methyl-alcoholic solution of ferrous chloride and ethylcarbylamine (3 mols.).

All these compounds are decomposed by alkalis, but the ferric compound exhibits its greater stability in giving a precipitate with sodium nitrate only in the presence of dilute nitric acid, and a brown Prussian blue only in the presence of hydrochloric acid. H. N. S.

**Cobalt Dioximines. II.** LEO TSCHUGAEFF (R. 1907, 36, 3498—3504. Compare Abstr., 1906, i, 814).—Since cobalt dioximines, which contain all the components of the complex molecules in the non-ionisable form, are of especial interest, the author describes two general reactions for preparing compounds of this type.

The compounds  $[\text{CoNH}_2\text{ClD}_2\text{H}_2]$  and  $[\text{CoD}_2\text{H}_2\text{NH}_2\text{NO}_2]$ ,  $\text{CoD}_2\text{H}_2 = \text{R}^1\text{C}(\text{N}=\text{OH})\cdot\text{C}(\text{N}=\text{OH})\cdot\text{R}^2$ , obtained by the reaction of dimethylglyoxime with derivatives of the pentammine series,  $[\text{Co}(\text{NH}_2)_5\text{Cl}]\text{X}_2$  and  $[\text{Co}(\text{NH}_2)_5\text{NO}_2]\text{X}_2$ , in the presence of excess of ammonium acetate have already been described.

It is found that the presence of an excess of acid is essential to the success of this reaction in order to prevent the formation of the derivative of the diamine series, thus:  $[\text{Co}(\text{NH}_2)_4\text{D}_2\text{H}_2]\text{X}_2 + \text{NH}_2\text{D}_2\text{H}_2\text{NH}_2 \rightarrow [\text{Co}(\text{NH}_2)_5\text{D}_2\text{H}_2]\text{X}_2$ .

Bromopentammine bromide reacts with dimethylglyoxime thus:  $[\text{Co}(\text{NH}_2)_5\text{Br}]\text{Br}_2 + 2\text{DH}_2 = [\text{CoNH}_2\text{BrD}_2\text{H}_2] + 2\text{NH}_2\text{BrD}_2\text{H}_2\text{NH}_2$ .

melting compounds are typical non-electrolytes and are very easily oxidised by air; they are soluble in dilute acetic acid in glistering, reddish-brown needles; its solution in concentrated sulphuric acid is red.

The compound  $[\text{CoNH}_3(\text{NO}_2)_2\text{D}_2\text{H}_2]$ , obtained by the interaction of the reaction or isoxantho-salts,  $[\text{CoNH}_3\text{NO}_2]\text{X}$ , and methylethylglyoxime, separates from alcohol in yellowish-brown crystals and is also a non-electrolyte. The compound  $[\text{CoNH}_3\text{D}_2\text{H}_2\text{Cl}]$  was also obtained from dimethylglyoxime and purpled cobalt chloride,  $[\text{CoNH}_3\text{Cl}]\text{Cl}$ . The reaction failed when an attempt was made to prepare the compound  $[\text{CoD}_2\text{H}_2\text{NH}_2\text{NO}_2]$ . The compound  $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2\text{NO}_2]$  was the only product of the action of dimethylglyoxime on the pentammine nitrate,  $[\text{CoNH}_3\text{NO}_2]\text{NO}_3$ .

The compound  $[\text{CoNH}_3\text{ID}_2\text{H}_2]$ , obtained from dimethylglyoxime and roseo-pentammine iodide,  $[\text{Co}_2\text{NH}_3\text{I}_2\text{O}_2]$ , crystallises in dark brown needles. The iodine atom in this compound is not so firmly bound as in the corresponding chloro and bromo compounds. When heated with dilute ammonia at  $100^\circ$ , it forms the compound  $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]$ , an iodide of the diammine series, which contains an uncombined iodine atom.

The behaviour of the roseo-iodide in comparison with the corresponding chloro and bromo-salts is remarkable, since the bromide reacts with dimethylglyoxime only traces of the compound  $[\text{CoNH}_3\text{ID}_2\text{H}_2]$ , whilst the roseo-chloride does not give the compound  $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]$ .

The pseudo-halogen salts of the tetrammine series,  $[\text{CoNH}_3\text{Cl}_2]\text{Cl}$ ,  $[\text{CoNH}_3\text{Br}_2]\text{Br}$ , behave towards dimethylglyoxime like the corresponding pentammine compounds, giving the compounds  $[\text{CoNH}_3\text{ID}_2\text{H}_2]$  and  $[\text{CoBrNH}_3\text{D}_2\text{H}_2]$ . The isomeric croceo- and green-salts appear to behave similarly, and are at present under investigation.

Another method for preparing the compounds in question is described. A process of autoxidation takes place between 1 mol. of cobalt salt and 1 mol. of dimethylglyoxime in alcoholic solution and in the presence of pyridine, or a similar base in the presence of air. The reaction of the compound  $[\text{CoClPyD}_2\text{H}_2]$  is expressed by the equation:  $2\text{C}_2\text{H}_4\text{O} + 4\text{DH}_2 + 4\text{Py} + \text{O} = 2[\text{CoClPyD}_2\text{H}_2] + 2\text{PyHCl} + \text{H}_2\text{O}$ . The reaction was also conducted with a picoline, isopimoline, and maline. In addition to the chlorine atom, there may be substituted other halogen atoms or the electronegative groups,  $\text{NO}_2$ ,  $\text{SCN}$ ,  $\text{NCO}$ ,  $\text{CN}$ ,  $\text{N}_3$ , etc. For dimethylglyoxime, other 1:2 dioximes, for example, ethylenediamineglyoxime, may be substituted. The compounds obtained are yellowish and brown to reddish brown in colour; they are soluble with difficulty and exhibit properties typical of non-electrolytes. The compound  $[\text{CoPyClD}_2\text{H}_2]$  forms yellowish-brown crystals. The compounds  $[\text{CoPySCNOD}_2\text{H}_2]$  and  $[\text{CoPyN}_3\text{D}_2\text{H}_2]$  are the first known derivatives of cyanic acid and hydrazoic acid respectively known, which are non-conductors. The compound  $[\text{CoPyN}_3\text{D}_2\text{H}_2]$  forms reddish-brown crystals and is very stable. The following derivatives of dimethylglyoxime have been prepared:  $[\text{CoNH}_3\text{ClD}_2\text{H}_2]$ ,  $[\text{CoNH}_3\text{BrD}_2\text{H}_2]$ ,  $[\text{CoNH}_3\text{ID}_2\text{H}_2]$ ,  $[\text{CoNH}_3\text{NO}_2\text{D}_2\text{H}_2]$ ,  $[\text{CoPyClD}_2\text{H}_2]$ ,

[CoPyID<sub>2</sub>H<sub>2</sub>], [CoPyNO<sub>2</sub>D<sub>2</sub>H<sub>2</sub>], [CoPySCND<sub>2</sub>H<sub>2</sub>], [CoPyN<sub>2</sub>D<sub>2</sub>H<sub>2</sub>], [CoPyN<sub>2</sub>D<sub>2</sub>H<sub>2</sub>], [Co isoquinoline ClD<sub>2</sub>H<sub>2</sub>], [Co acridine ClH<sub>2</sub>].

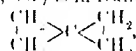
The following derivatives of methylethylglyoxime have been prepared: [CoNH<sub>2</sub>NO<sub>2</sub>D<sub>2</sub>H<sub>2</sub>] and [CoPySCND<sub>2</sub>H<sub>2</sub>]. The following derivative of methylethylglyoxime has been prepared: [CoClNH<sub>2</sub>D<sub>2</sub>H<sub>2</sub>].

A. M. K.

**Action of Nitrous Oxygen Compounds with Organic and magnesium Compounds.** IWAN J. BEWAD (*J. Chem. Soc.*, 1907, 39, 947-973. Compare Abstr., 1906, (this vol., i, 671). The group -NO in organic nitrites behaves like zinc alkyls similarly to the -CO group in aldehydes, nitrosyl chloride and zinc ethyl react thus:  $\text{ONCl} + \text{ZnEt}_2 \rightarrow \text{ZnEt} \cdot \text{O} \cdot \text{NEt}$ , from analogy to  $\text{OCCl}_2$  which reacts with  $\text{OH} \cdot \text{CEt}_2$ . The  $\beta$ -diethylhydroxylamine thus produced reacts with the product obtained by the action of zinc ethyl on nitrites. An abstract of the rest of this paper has already appeared (this vol., i, 671).

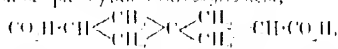
Z. K.

**Spirocyclanes.** HERMANN FECHT (*Ber.*, 1907, 40, 188-193. Compare Bayer, Abstr., 1901, i, 135, for nomenclature). Spiromethylene (Abstr., 1896, i, 669) is in reality spiro-pentane,



for the nitrile, obtained from its dibromide, yields on hydrolysis *aa-ethyleneglutamic acid*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} > \text{C} < \text{CO}_2\text{H} \end{array} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which is identical with the acid prepared from ethyl glutaconitrile and sodium ethoxide in alcoholic solution.

The reaction between pentaerythritol tetrabromohydrin and methyl malonate in boiling anhydrous alcoholic solution leads to the formation of spiro-pentane-carboxylic acid,



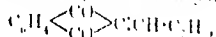
m. p. 216°, which is stable to potassium permanganate and hydrobromic acid at 150°, and fused potassium hydroxide.

Pentaerythritol tetrabromohydrin, benzene, and aluminium chloride react on the water-bath to give, in very bad yield, *xylylenefluorene*, m. p. 148°, and a pale yellow, fluorescent substance,

m. p. 161°. The formula  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} > \text{C} < \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} < \text{C}_6\text{H}_4 \\ | \\ \text{CH}_3 \end{array}$  is assigned to either of the substances, because their properties are similar to those of *xylylenefluorene*,  $\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} > \text{C} < \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} < \text{C}_6\text{H}_5 \end{array}$  m. p. 125°, which is prepared from fluorene, *o*-xylylene dibromide, and potassium oxide at 250°, crystallises in colourless, refractive crystals, stable to acids or alkalis.

*Xylylenediketohydrofluorene*,  $\begin{array}{c} \text{CO} \\ | \\ \text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} > \text{C} < \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} < \text{C}_6\text{H}_4 \\ | \\ \text{CO} \end{array}$  is obtained by the addition of an alcoholic solution of sodium cyanide

to *p*-xylene dibromide and diketohydrindene dissolved in ethyl acetate, it crystallises in yellow needles, decomposes by warming with alkalis, develops a violet colour with concentrated sulphuric acid, and in hot alcoholic solution changes to a yellow polymeride, m. p. 215° (decomp.). The *dioxime* has m. p. 215°; the yellow *phenylhydrazide* has m. p. 177°, and the brown *diphenylhydrazone*,  $C_{22}H_{14}N_4$ , has m. p. 225°. 2-*o*-Methylphenylene diketohydrindene,



m. p. 171°, forms pale yellow needles, gives a yellow colour with concentrated sulphuric acid, and does not show any tendency to polymerise.

C. S.

### Preparation of *tert*-Butyltoluene and *tert*-Butylxylene.

ACETES-GESellschaft für ANILIN-FABRIKATION (D.R. P. 184230).—*tert*-Butylxylene, employed in the production of artificial musk, is obtained in almost theoretical amount by passing *isobutylene* gas through a mixture of *m*-xylene and aluminium chloride to which some *o*-cetyl chloride has been added, or into which hydrogen chloride has been introduced. *Isobutyl* bromide or hydrogen bromide may also be employed to start the reaction, and *tert*-butyltoluene may be prepared in a similar manner. The aluminium chloride may be replaced by other condensing agents, such as the chlorides of manganum, zinc, or iron; the corresponding bromides may also be employed.

G. T. M.

### Reactions with Amorphous Phosphorus. III. Action of Amorphous Phosphorus and Hydrochloric Acid, D 1-19, on Nitrobenzene. THEODOR WEYL (*Ber.*, 1907, 40, 3608–3612, compare this vol. i, 118, 395).—Nitrobenzene is reduced to only a

very small extent when heated with red phosphorus and hydrochloric acid, D 1-19, at temperatures not above 140°, but at 140°–160° considerable amounts of aniline and *p*-chloroaniline are formed. In the experiment, 7% of the nitrobenzene entering into the reaction was *p*-chloroaniline.

Aniline and *p*-chloroaniline do not form chloroaniline when heated with phosphorus and hydrochloric acid, D 1-19, at temperatures not above 140°, but according to Bamberger, Bisdorf, and Szolayski (*Ber.*, 1906, 39, 341) *p*-chloroaniline is formed by the action of hydrochloric acid on phenylhydroxylamine or on nitrosobenzene, and some of these substances must be formed intermediately in the reduction of nitrobenzene by phosphorus and hydrochloric acid.

*Nitrobenzene* gives the well-known violet-purple coloration with ferric chloride in aqueous, but a yellow coloration in acetone, solution, and *m*-chloroaniline give no coloration in aqueous, but a yellowish brown in acetone, solution, and *p*-chloroaniline gives a reddish brown in both solvents.

*Nitroacetanilide* has m. p. 182° (172.5°; Beilstein and Kurbatoff, *Monatsh.*, 1877, 5, 473).

G. Y.

**Mercury Derivatives.**—An aqueous suspension of *o*-nitroaniline heated for eight hours with freshly precipitated mercuric oxide and 30% sodium hydroxide solution, or an equivalent amount of any other alkali hydroxide or carbonate, furnishes a mercury derivative soluble in aqueous alkali hydroxides and precipitated as a very voluminous, yellow mass on addition of dilute acids, including acetic acid. The *hydrochloride* of this product is obtained in a crystalline form in colourless needles, m. p. 145—158°, by precipitating an ammoniacal solution with hydrochloric acid. The compound contains mercury and *o*-nitrotoluene in the proportion of one atom of the latter to two molecules of the latter.

A sparingly soluble *dimercury* derivative is obtained by heating the boiling with mercuric oxide until a product insoluble in hydrochloric acid is obtained. The new compound contains a *o*-nitrotoluene residue combined with two atomic proportions of mercury. The sparingly soluble pale yellow chloride is decomposed by an aqueous sodium hydroxide, the free dimercury derivative is obtained in dilute acetic acid, and reprecipitated by alkali as a heavy, crystalline, yellow mass, which explodes on heating, and when warmed decomposes above 220° without melting. It also explodes on dilute nitric or sulphuric acid, but is insoluble in ammonium

**Salts and Esters of Benzenesulphonitroanilide.**—S. O. Ber. (Ber., 1907, 40, 3528—3536).—Benzenesulpho-*o*-nitroanilide, m. p. 102—103.5°, forms pale yellow or almost colourless, microscopical crystals and dissolves in alcohol or benzene with a yellow coloration. The *ammonium* salt is yellow; the *sodium* salt orange, m. p. 210°, is a red liquid; when freshly made and cooled to -70° it becomes yellow. The same yellow salt is formed on the addition of sodium to a cooled ethereal solution of the *o*-nitroanilide; it becomes orange when rubbed with a glass-rod, but is obtained in silky, glistening yellow needles when slowly crystallised, or in the orange modification when crystallised quickly.

The *thallium* salt is likewise orange when prepared warm and red when made at lower temperatures; it melts to a red liquid at 150°, which becomes orange again when it solidifies.

The *lithium*, *potassium*, *rubidium*, and *mercury* salts were obtained in one, the yellow, form only; the *silver* sodium double salt is yellow.

*Benzenesulphomethyl-o-nitroanilide*,  $C_6H_4SO_2NMeCH_2HNO_2$ , forms colourless crystals, m. p. 116—117°, and gives colourless solutions.

*Benzenesulpho-m-nitroanilide* forms colourless crystals, m. p. 136—137° (Leilmann, Abstr., 1883, 807, describes it as yellow crystals, m. p. 131—132°). The *ammonium* salt is yellow, like the *sodium* and *potassium* salts, which retain this coloration on heating and show no tendency to form the red modification. The *benzenesulphomethyl-m-nitroanilide* is colourless, m. p. 82—83°. It is soluble

is colourless and loses yellow tints only the methyl ester, m. p. 120—121°, is also colourless.

Both the *o*- and *p*-benzenesulphonitroanilides are converted by nitric acid into the same *trinitro*-derivative,  $C_6H_3SO_3NH \cdot O_2H(NO_2)_3$ , m. p. 310—311°, crystallising in almost colourless needles which give yellow solutions in acetone.

E. F. A.

**Action of Phosphorus Oxychloride on 1-Naphthylamine 8-sulphonic Acid.** FREDERIC DANNEKEH (*J. Amer. Chem. Soc.*, 1907, 29, 1317—1328).—On heating 1-naphthylamine 8-sulphonic acid with concentrated sulphuric acid, Dressel and Kothe (*Abstr.*, 1894, i, 608) obtained the sulphonic acid of an inner anhydride which they termed *naphthasultam*. They were unable to obtain the *naphthasultam* itself, since the anhydride formation was always accompanied by sulphonation at the nucleus. This has now been effected, however, by the action of phosphorus oxychloride on potassium 1-naphthylamine 8-sulphonate, a *nitro*-derivative of the theoretical being obtained.

1-*N*-*naphthasultam*,  $C_{10}H_6 \begin{smallmatrix} SO_2 \\ \diagup \\ NH \end{smallmatrix}$ , m. p. 177—178°, crystallises from at water in needles and dissolves in many organic liquids to form solutions with an apple-green fluorescence. The *methyl* derivative, m. p. 145°, and the *ethyl* derivative, m. p. 85°, are crystalline, and give fluorescent solutions; the former, when heated with potassium cyanide, is converted into 1-methylnaphthylamine 8-sulphonic acid, proving that the methyl group is attached to the nitrogen atom. Oxidation with potassium dichromate and ferric chloride, and treatment with nitrous acid is converted into a red, crystalline substance. The *sodium* salt condenses with diazo compounds to form *nitro*-derivatives. *1-Naphthasultam*, m. p. 235°, is a white compound which melts when boiled with alcohol. *Nitronaphthasultam*, m. p. 263°, forms six-sided prisms, this compound can also be prepared by the nitration of 1-*N*-*naphthasultam* 2:4-disulphonio (*J. Dressel and Kothe, loc. cit.*). 2:4-*Diamino*-1:8-*naphthasultam* (*nitro*-derivative, m. p. 239°, forms slender, pale yellow needles, and when 1-*N*-*naphthasultam* is boiled with acetic anhydride, 1:8-*iso*-

*naphthasultam*,  $C_{10}H_6 \begin{smallmatrix} SO_2H \\ \diagup \\ N \end{smallmatrix}$ , is produced, which forms rhombic crystals with a yellow *sodium* salt. When a solution of this compound in methyl alcohol is treated with hydrogen chloride, a *chloro*-*naphthasultam*, m. p. 200—201°, is produced; the same substance can be obtained by the action of chlorine on *isonaphthasultam*. The *bromo*-*naphthasultam*, m. p. 162°, is a white, crystalline substance. The *nitro*-*naphthasultam*, m. p. 212°, forms pale yellow crystals. 2:4-*Dinitro*-1:8-*iso*-*naphthasultam*, m. p. 256°, forms yellow crystals; if this compound is treated with sodium hydroxide and the product acidified, the "normal" *naphthasultam* is produced.

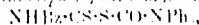
By the action of fuming nitric acid on either *naphthasultam* or *iso*-



naphthasultam, 1:3-dinitronaphthalene-5-sulphonic acid is a solid which does not melt but explodes at about 300°. 1:3-Nitro-4-amino-5-sulphonic acid forms black needles, and decomposes when heated.

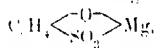
**Thiocyanates and isothiocyanates (Thiocarbimides).**—**Diphenylcarbamyl Thiocyanate.** TREAT B. JOHNSON and LEVY (*Amer. Chem. J.*, 1907, 38, 456—461).—When an alkyl isocyanate is treated with ammonium or potassium thiocyanate, an alkyl isothiocyanate is first produced, although it sometimes undergoes rearrangement to the corresponding thiocarbimide. In the case of the aromatic isocyanates, however, the products of the reaction have always been thiocarbimides. It has now been found that diphenylcarbamyl isocyanate reacts smoothly with potassium thiocyanate with formation of diphenylcarbamyl thiocyanate, and it is considered probable that other carbamyl chlorides examined by Dixon (*Trans.*, 1895, 67, 100; 1900, 60, 855, 1593; 1901, 85, 807) would also yield thiocyanates by reaction with potassium thiocyanate under suitable conditions.

*Diphenylcarbamyl thiocyanate*,  $\text{NPh}_2\text{CO}:\text{SCN}$ , m. p. 155°, prismatic crystals, is not affected by hot concentrated sulphuric acid, and does not react with ammonia or aniline at the ordinary temperature. When heated with thiobenzic acid, carbon dioxide is evolved and *benzoyldithiodiphenylcarbamyl carbamate*,



m. p. 128—129°, is produced, which crystallises in prisms. *Diisodiphenylamine*, m. p. 177°, is also formed in this reaction, and separates from alcohol in prismatic crystals. The thiocyanate does not show any tendency to undergo rearrangement at the ordinary temperature, but when heated at 150—160°, a thiocarbimide is produced, which reacts with ammonia to form diphenylthiocarbimide.

**Action of Sulphuric Acid on Phenol.** JULIUS OGGER (*Ber.*, 1907, 40, 3633—3647). Kekulé (*Ber.*, 1869, 2, 330) found that the action of concentrated sulphuric acid on phenol at the ordinary temperature leads to the formation of the ortho, together with a little of the para, -sulphonic acid, whilst at 100—110° the para acid is formed. Later authors (Engelhardt and Latschinow, *Ber.*, 1868, 4, 77; Pogg., this Journ., 1876, i, 388) have been unable to separate the two sulphonic acids completely by Kekulé's method. The present author has found that the two isomerides may be separated readily by means of the barium or magnesium salts. On cooling of the aqueous solution of the monobarium salts, the ortho-*o*-sulphonate crystallises out, and the para acid may be isolated from the mother liquor by conversion by means of magnesium chloride into the monomagnesium salt,  $(\text{OH}:\text{C}_6\text{H}_4:\text{SO}_3)_2\text{Mg}$ , which crystallises on further evaporation. The monomagnesium *o*-sulphonate crystallises only with great difficulty, whilst the dimagnesium salt,



is only sparingly soluble; the magnesium salts of the para acid have the converse solubilities.

Contrary to Kerné's statements, the *o*-sulphonic acid is not converted into the para-isomeride on prolonged boiling with water, and is only partially transformed on prolonged treatment with concentrated sulphuric acid at the ordinary temperature. The two isomerides form an equilibrium dependent on the temperature and concentration, the formation of the ortho acid being favoured by low temperatures and dilution of the sulphuric acid. It is probable that between 100–110° the ortho-acid is not transformed completely. The alkali, alkaline earth, lead, and zinc salts of the pure *o*- and *p*-sulphonic acids, and of phenol 2:4 disulphonic acid, are described.

The reaction solution after removal of the *o*- and *p*-sulphonic acids and the 2:4 disulphonic acid, which is formed readily in presence of an excess of sulphuric acid, contains small amounts of an acid, probably phenol-sulphonic acid (Solomonoff, *Zeitsch. Chem.*, 1863, 5, 229). This has been isolated in the form of its *monomethinium*, *monochloride*, and *mononitrate*,  $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{M})_2\cdot\text{NH}_4\text{O}$ , salts, which are described. These three salts give a violet coloration with ferric chloride.

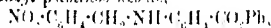
Mercapto-septol," which is stated to be a 33% aqueous solution of phenol-sulphonic acid, is found to be a solution of the *p*-sulphonic acid and an amount of the ortho-acid equal to about 6% of the para-acid.  
G. Y.

**Action of *p*-Nitrobenzyl Chloride on *p*-Aminophenol.** MAXIM BAKENIN and C. PROCTOR (*Chem. Zvesti.*, 1907, 37, ii, 240–250; *Chem. Abstr.*, 1906, i, 196). As already stated (*loc. cit.*), the condensation of *o* or *p*-aminophenol with benzyl chloride yields mono- or disubstituted derivatives in which the benzyl groups must be regarded as united directly with the amino-nitrogen. By the interaction of *p*-aminophenol (1 mol.) and *o*-nitrobenzyl chloride (2 mols.) in alcoholic solution and in presence of sodium acetate, Lehmann and Mayer (Astr., 1893, i, 198) obtained a compound to which they ascribed the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ; from the above results, it must be held that substitution occurs in the amino and not in the hydroxyl group of the *o*-aminophenol.

*o*-Nitrobenzyl *p*-aminophenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , obtained by the interaction of *p*-nitrobenzyl chloride and *p*-aminophenol in alcoholic solution, crystallises from water in silky, yellow, hydrated ( $+ \text{H}_2\text{O}$ ) needles; from alcohol in yellow, micaceous, hydrated ( $+ \text{H}_2\text{O}$ ) scales, m. p. 86–87°, and from anhydrous benzene or chloroform in rhombic crystals, m. p. 114–115°. The hydrochloride,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_2\cdot\text{HCl}$ , m. p. 101°.

*o*-Nitrobenzyl *p*-aminophenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , also obtained by the reaction between *p*-nitrobenzyl chloride and *p*-aminophenol in alcohol, separates from alcohol in red, acicular crystals, m. p. 150–151°. The hydrochloride,  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_3\cdot\text{HCl}$ , m. p. 202°, is readily hydrolysed by water.

*Di-*p*-nitrobenzyl *p*-aminobenzonitrile.*



Prepared by the interaction of *p*-nitrobenzyl chloride and *p*-amine-

phenyl carbamate,  $\text{C}_6\text{H}_5\text{NHCOC}_6\text{H}_5$ , m. p. 21—22°. The hydrochloride,  $\text{C}_6\text{H}_5\text{NHCOC}_6\text{H}_5 \cdot \text{HCl}$ , m. p. 110—112°, readily undergoes change.

**Benzoyl-*p*-nitrobenzyl-*p*-aminophenol**,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NBz} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , prepared by the action of benzoyl chloride on *p*-nitrobenzyl-*p*-aminophenol in benzene solution, crystallises from alcohol in yellow needles, m. p. 208—210°.

*p*-Nitrobenzyl-*p*-aminophenol gives a violet coloration with ferric chloride and water and a red coloration with Liebermann's reagent and acetic acid. Di-*p*-nitrobenzyl-*p*-aminophenol, being insoluble in water, gives no colour with ferric chloride and water, but with ferric chloride gives a violet coloration; both the base and its hydrochloride give a red colour with Liebermann's reagent and acetic acid. Neither phenyl *p*-nitrobenzyl-*p*-aminobenzoate nor its hydrochloride gives coloration with ferric chloride, but both yield red coloration with Liebermann's reagent. Benzoyl-*p*-nitrobenzyl-*p*-aminophenol gives coloration with ferric chloride, possibly owing to its insolubility; it yields the characteristic red coloration with Liebermann's reagent.

**Binary Solution Equilibrium between Carbamide and the Three Isomeric Cresols.** ROBERT KREMANNS (*Monatsh.*, 1907, 38, 1125—1136. Compare Abstr., 1906, ii, 268).—The melting-point curve for mixtures of carbamide and *p*-cresol falls from the m. p. of carbamide to a break at 25.5°, and then to a eutectic point at 21.5°, representing mixtures containing 21.5 mol. % and 15 mol. % of carbamide respectively; within these limits of temperature and concentration, carbamide and *p*-cresol form a molecular compound. Mixtures of *p*-cresol carbamide and carbamide and of *p*-cresol and carbamide exist in the solid phase below 25.5° and 20° respectively; above these temperatures, but below the m. p.'s of carbamide and *p*-cresol, the liquid phase is in contact with the one solid component.

Carbamide forms molecular compounds in the same manner within wider limits of temperature and concentration with *m*- and *o*-cresols. The melting point curve for mixtures of carbamide and *o*-cresol falls from the m. p. of carbamide to a break at about 26°, and then to a eutectic point at about 26°, representing mixtures containing approximately 27.8 mol. % and 19 mol. % of carbamide respectively. The melting-point curve for mixtures of carbamide and *m*-cresol falls to a break at about 65°, and then to a eutectic point at about 2.5°, representing mixtures containing approximately 65 mol. % and 2 mol. % of carbamide.

**Derivatives of 6-Nitro-1:3:4-xenol.** RALPH W. HARTLEY (*Gazetta*, 1907, 37, ii, 284—288).—6-Nitro-4-methoxy-1:3:4-xenol,  $\text{C}_6\text{H}_3\text{NO}_3$ , prepared by oxidising the methyl ether of 6-nitro-1:3:4-xenol with potassium permanganate, crystallises in white, slender, silky needles, m. p. 230°. The dimethyl ester,  $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_6$ , separates from methyl or ethyl alcohol in minute, hard crystals, m. p. 118°. The monomethyl ester,  $\text{C}_{10}\text{H}_7\text{NO}_5$ , crystallises in minute, white needles, m. p. 190°; the other

white, colorless crystals, m. p. 108°. The base,  $C_{10}H_7O_2N$ , is obtained from the salt,  $C_{10}H_7O_2N \cdot HCl$ , as a white, crystalline powder, m. p. 108°. The sodium salt,  $C_{10}H_7O_2Na$ , is obtained as a yellow, anhydrous, crystalline powder.

The two *nitromethoxy-m-toluic acids* ( $NO_2 : OMe = 6 : 4$  and  $4 : 6$ ) have been prepared, but not distinguished. One of them,  $C_{10}H_7O_2N$ , separates from water or aqueous alcohol as a yellowish-white powder, m. p. 174°, which is gradually turned red by the action of light; the other isomer, m. p. 170° (decomp.), is white, and does not redden under the action of light.

T. H. P.

**Isomerism with Schiff's Bases.** OTTO ANSELMINO (*Ber.*, 1907, 40, 346-3474).—The author has shown previously (*Abstr.*, 1906, 1, 131) that *phomosalicylaldehydeanil* occurs in two forms, a yellow and a red, which by crystallisation at definite temperatures can be converted one into the other; when dry, the yellow form can be converted into the red, but the reverse change cannot be effected with the dry substance. The effect of pressure is the same as that of heat.

Efforts are submitted to show that these forms are isomeric and not polymorphous. Density determinations gave different values for the two forms, thus, for the yellow form,  $D^{20}_4$  was 1.243, and for the red form 1.261. Solubility determinations in 95% alcohol were carried out at temperatures from 11.8° to 50°. Measurements of the heat of solution in benzene were also made, and the absorption spectra studied. The conclusion is drawn that solutions below 33° contain the yellow form, and above 34° the red.

The behaviour of the anil towards acetyl chloride, acetic anhydride, benzoyl chloride, methyl sulphate, and phenylcarbimide is indicated. When the Grignard action is applied, unchanged anil is obtained at temperatures below 30°; above 40°, the red variety is transformed by the Grignard reagent, but the yellow variety is not. The same remarks with regard to Grignard's reagent hold with *salicylaldehydeanil*; it is known only in the yellow form, and does not react, whereas its methyl ether does.

The product obtained from the yellow form differs in tint from that obtained from the red form.

The conclusion is drawn that all yellow anils have a similar structure, whereas the red anil in question has the configuration of its isomer. Crystallographic measurements also confirmed this view.

The crystalline form of *salicylaldehydeanil* differs from that of *anil* (m. p. 108°).

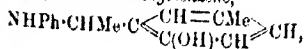
The derivatives of *o-hydroxy-m-methylbenzylideneaniline*,



separate from light petroleum in needles, m. p. 161°.

The *o-methylbenzylideneaniline*,  $C_{15}H_{13}ON$ , prepared by the action of methyl sulphate at 49° on the anil, separates from light petroleum in yellow needles, m. p. 76°.

The *o-methyl-a-anilinoethylbenzene*,



obtained by the action of magnesium methyl iodide on the 12, separates from light petroleum in colourless, rectangular plates, m. p. 98°.

*o*-Methoxy-*m*-methyl-*a*-anilinoethylbenzene,  $C_{16}H_{19}ON$ , obtained from magnesium methyl iodide and the methylated anil, separates from light petroleum in glistening crystals, m. p. 78°.

*o*-Hydroxy-*m*-methyl-*a*-acetylaniethylethylbenzene,  $C_{17}H_{19}ON$ , separates from light petroleum in nodular crystals, m. p. 123°.

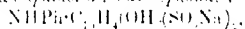
*o*-Methoxy-*m*-methyl-*a*-acetylaniethylethylbenzene,  $C_{18}H_{21}ON$ , separates from light petroleum in nodular crystals, m. p. 123°.

*a*-Anilino-*o*-ethylanisole,  $C_{17}H_{19}ON$ , separates from light petroleum in pyramids, m. p. 45°.

**Preparation of Aminonaphthols.** FRANZ SACHS (Ber., 1907, 181333). The aminonaphthols can be obtained by heating  $\beta$ -naphthols or their alkali derivatives with sodamide at 200°. The use of the latter compounds reduces the proportion of alkali required. Naphthalene, quinoline, paraffin, and other hydrocarbons are employed as diluents. Under these conditions, 1-naphthol furnishes 5-amino- $\beta$ -naphthol, whilst  $\alpha$ -naphthol yields 1-amino- $\alpha$ -naphthol (compare Abstr., 1906, i, 829 and 949).

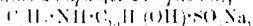
**Preparation of 8-Arylamino- $\alpha$ -naphtholsulphonic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R. P. 185,475). The 8-amino- $\alpha$ -naphtholsulphonic acids when heated with primary amines and their dry hydrochlorides give rise only to tar, but when these acids or their alkali salts are heated with secondary amines in the presence of water, the hitherto unknown 8-arylamino- $\alpha$ -naphtholsulphonic acids are obtained.

*Sodium 8-anilino- $\alpha$ -naphthol-3:6-disulphonate,*



produced by heating sodium 8-amino- $\alpha$ -naphthol-3:6-disulphonate with aniline and water at 120° for forty-eight hours, crystallises from water in spherical aggregates of white needles; the sodium sulphate salt separates in felted white needles.

*Sodium 8-*p*-tolylamino- $\alpha$ -naphthol-1-sulphonate,*



prepared in a similar manner from sodium 8-amino- $\alpha$ -naphthol-4-sulphonate, *p*-toluidine, and water, crystallises in needles; the free acid separates in felted white needles. The patent contains a tabulated description of ten 8-arylamino- $\alpha$ -naphtholsulphonic acids and other sodium salts.

**1:2-Methylnaphthalene quinol.** GERDO BARCELON (Ann. Chim. Silvestri (Atti R. Accad. Lincei, 1907, [v], 16, no. 2, 1907). Compare this vol. i, 862).—1-Methyl- $\beta$ -naphthol, when heated with acetic acid solution with chromic acid, yields 1:2-methylnaphthalene quinol (compare Fries and Habner, Abstr., 1906, i, 130).

**6-Bromo-2-methoxy-1-methyl-naphthalene,**  $C_{16}H_{13}BrMeO$ , crystallises from acetic acid in white needles, m. p. 65°. (Fries and Habner, *loc. cit.*).

**1-methylnaphthalene**,  $C_{11}H_8$ ,  $\begin{matrix} \text{OMe} \cdot \text{C}(\text{N} \cdot \text{Ph}) \\ | \\ \text{OH} = \text{OH} \end{matrix}$ , prepared

by the action of phenylhydrazine on 1:2-methylnaphtha- $\psi$ -quinol, obtained from alcohol in orange-red scales, m. p. 79°–80° (decomp.), soluble in ether, ethyl acetate, chloroform, or acetone, and dissolves in concentrated hydrochloric or sulphuric acid to a red solution.

**1-methylphthalazocarboxamide**,  $C_{11}H_8 \begin{matrix} \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{CO} \cdot \text{NH}_2 \\ | \\ \text{CH} = \text{CH} \end{matrix}$ , pro-

duced by the action of semicarbazide on 1:2-methylnaphtha- $\psi$ -quinol, obtained from water in orange needles, m. p. 143°–144° (decomp.), soluble in ether, acetic acid, or chloroform, and dissolves in concentrated hydrochloric or sulphuric acid giving a green coloration which rapidly turns red.

**1:2-methylnaphtha- $\psi$ -quinoline**,  $C_{11}H_8 \text{Me}(\text{OH}) \cdot \text{NOH}$ , separates in ethyl acetate in crystals, m. p. 140° (decomp.), and dissolves easily in chloroform, benzene, carbon disulphide, or alcohol, and is sparingly soluble in petroleum. By acetic acid, it is decomposed probably in a manner similar to the oxime of dimethylnaphtha- $\psi$ -quinol (compare *Annalen*, 1896, i, 488), yielding 2-nitroso-methylnaphthalene. Reduction of the oxime by means of zinc dust and hydrochloric acid yields 1-methyl-2-naphthylamine and its acetyl derivative (compare Fries and Hubner, *loc. cit.*). **1-Methyl-2-naphthylamine hydrochloride** separates in shining scales, m. p. 215° (decomp.). T. H. P.

**Condensation Products of Formaldehyde.** J. BRISLAUER and A. FRIEDL (Ber., 1907, 40, 3781–3786).—Methylphthalimide is obtained by heating phthalimide with a 10% solution of formaldehyde in a 25-31 tube at 150°–160°; similarly, methylenbis-uccinimide (Ber., Abstr., 1891, i, 488) is obtained from formaldehyde and succinimide.

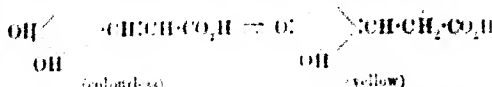
**Methoxyphenyl methyl ether**,  $\text{O}(\text{Ph})\text{CH}_2\text{OMe}$ , is produced by the action of phenol and formaldehyde in the presence of sulphuric acid, and by the action of monochloromethyl ether on potassium succinimide. It is a colourless liquid, b. p. 197°–200°,  $D_4^{20}$  1.0814, and reacts with bromine water to a *para* derivative,  $C_{10}H_9O_2\text{Br}_2$ , which separates in colourless, silky needles, m. p. 112°–113°.

The action of formaldehyde on naphthol in the presence of sodium carbonate results in the formation of a substance,  $C_{22}H_{16}O_3$ , which is a dark brown, amorphous, infusible powder. This on distillation yields a substance,  $C_{22}H_{16}O$ , which forms small, pale yellow crystals, m. p. 72°–80°, and gives a deep blue coloration with ferric chloride. W. H. G.

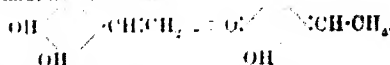
**Action of Benzyl Chloride on Resorcinol and Catechol.** G. F. LATTES and P. ARIZZO (Gazzetta, 1907, 37, ii, 250–252).—The action of benzyl chloride and resorcinol in benzene solution in the presence of zinc yields: (1) a compound,  $C_{13}H_{12}O_2$ , crystallising in slender needles, m. p. 74°–76°, soluble in benzene and carbon tetrachloride; (2) a compound crystallising in nacreous laminae, m. p. 203°–206°, soluble in benzene, insoluble in carbon tetrachloride, and containing 2.96% of carbon; (3) an oily compound,  $C_{16}H_{14}O_2(\text{CH}_2\text{Ph})_2$ .

**Cyclic Carbonic Esters of Vinylicatechol.** HANSEN, PETER and KARL NEUMAN (*Ber.*, 1907, 40, 3488—3498).—Paufler has already shown (this vol., i, 709) that the cyclic esters of catechols are suitable for the isolation of the latter and that protocatechualdehyde carbonate,  $\text{HO-C}_6\text{H}_3\text{<O>CO}$ , is suitable for the carrying out of syntheses in the catechol group.

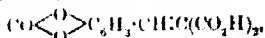
Vinylicatechol carbonate,  $\text{CO<O>C}_6\text{H}_3\text{-CH=CH}_2$ , is now described, being obtained from protocatechualdehyde carbonate by means of the corresponding benzylidene-malonate. The latter compound (colourless) is converted by aqueous pyridine into malonic acid (yellow), thus:  $\text{CO<O>C}_6\text{H}_3\text{-CH=CHCO(CO}_2\text{H)}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_3\text{(OH)}_2\text{-CH=CHCO}_2\text{H} + 2\text{CO}_2$ . The yellow tint of the latter acid is attributed to its partly undergoing the transformation:



Evidence is submitted to show that the free vinylicatechol is an equilibrium mixture of the forms:



**3:4-Dioxybenzylidenemalonate, carbonic acid carbonate,**



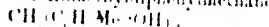
obtained by heating protocatechualdehyde carbonate, malonic acid, and anhydrous formic acid for nine to ten hours at about 65° in the absence of moisture, separates from glacial acetic acid in colourless needles, m. p. 197° (corr., decomp.), and is sparingly soluble in cold water; its aqueous solution exhibits a violet fluorescence; its solution in concentrated sulphuric acid is lemon-yellow. When boiled with acetic anhydride, it evolves carbon dioxide vigorously and gives a compound, m. p. about 245°. On account of the sensitiveness of the CO<sub>2</sub> group, the acid could not be further characterised by means of its salts.

**Vinylicatechol carbonate**, prepared by the dry distillation of the preceding acid in an apparatus which is described in detail, separates from a mixture of light petroleum and ether in colourless, glistening plates, m. p. 65°—66°; it has a very intense odour. Although it decolorises a solution of bromine in carbon disulphide almost immediately, a dibromide could not be obtained on account of the ease with which hydrogen bromide is eliminated after the addition. It gives a brownish-yellow coloration with ferric chloride and a violet-brown

reduction with sodium carbonate; its solution in concentrated sulphuric acid is reddish-orange. Its solution in alkalis is dark yellow. A. McK.

**Reduction of Saffrole and isoSaffrole.** J. TH. HENRIARD (*Chem. Weekblad*, 1907, 4, 630—633. Compare Klages, Abstr., 1899, i, 685; Chasman and Silber, Abstr., 1890, 965, 966, 1294; Eykman, Abstr., 1890, 244; and Jacobsen, Abstr., 1878, 732. The author has reduced saffrole and isosaffrole with nickel and hydrogen by Sabatier and Senderens's method. The reduction was never quantitative, the product always containing unchanged saffrole or isosaffrole. The reaction product was agitated with dilute sodium hydroxide, and the residual oil, containing unchanged saffrole and isosaffrole along with the reaction-product, fractionated, the bulk distilling at 228°. The residual liquid contained *m*-propylphenol, formed by reduction of the dihydro-saffrole with elimination of the para hydrogen atom. The *m*-propylphenol could not be obtained crystalline, although Jacobsen gives it as p. 26. A. J. W.

**Formation of Dihydroxydiphenylmethanes.** KARL AUWERS (and, in part, FR. JESCHKE and C. KRIEKE (*Annalen*, 1907, 356, 124—151). It has been shown previously that hydroxybenzyl bromides and their transformation products readily undergo reactions, leading to the formation of substances formulated at first as derivatives of stilbene, but later considered to be derivatives of diphenylmethane (Abstr., 1903, i, 631, 1201, 4, 487). The constitution of only one of these derivatives, 3:5:3':5'-tetrahydro-4:4'-dihydroxydiphenylmethane formed from 3-bromo-4-hydroxybenzyl bromide, has been definitely established. As some of these derivatives decompose into compounds containing a single benzene nucleus, and that with increase not to be expected of derivatives of diphenylmethane, it was necessary to establish the constitution also of one of these comparatively unstable products. This has been achieved now in the case of the product obtained from 3-bromo-4-hydroxy-2:5-dimethylbenzyl bromide, already shown (*loc. cit.*) not to be identical with 4:4'-dihydroxytetramethylstilbene. It is now found identical with 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane,



prepared by diazotisation of 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane,  $\text{CH}_3\text{C}_6\text{H}_3\text{Me}_2\text{N}(\text{H})_2\text{C}_6\text{H}_3\text{Me}_2\text{N}(\text{H})_2$ , which is obtained by transformation of methylenedi-*p*-xylylamine,  $\text{CH}_2(\text{NH}_2\text{C}_6\text{H}_4\text{Me}_2)_2$ .

**Methylenedi-*p*-xylylamine**,  $\text{C}_{12}\text{H}_{16}\text{N}_2$ , prepared by shaking *p*-xylylene with formaldehyde in aqueous solution, crystallises in glistening needles, m. p. 67—68°, and when heated with 2 mols. of *p*-xylylene in benzene and  $\frac{1}{2}$  mol. of *p*-xylylene in a reflux apparatus on the water bath, is transformed into 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane,  $\text{C}_{12}\text{H}_{16}\text{N}_2$ , which separates from benzene as a colourless, crystalline powder, m. p. 138—139°. When diazotised with sodium nitrite and boiled in hydrochloric acid solution, this yields 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane, m. p. 181°.

The following substances were prepared in the course of endeavours



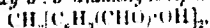
3:5-Dibromo-4-methoxybenzyl bromide,  $C_{10}H_7Br_2O$ , prepared by the action of hydrogen bromide on 3:5-dibromo-4-methoxybenzyl methyl ether in glacial acetic acid solution, crystallises in yellow needles, m. p. 66–67°. 4:4'-Dimethoxybenzophenone, m. p. 143–144°, is readily obtained by the action of carbonyl chloride on anisole in carbon tetrachloride solution in presence of aluminium chloride. The action of methylal on *p*-xylene in glacial acetic-sulphuric acid solution leads to the formation of a substance,  $C_{12}H_{16}O$ , m. p. 149°, the comparatively high temperature at which this melts makes it probable that it is not dioxylmethane. On treatment with cold fuming nitric acid, it yields a yellow, crystalline derivative, m. p. 183°.

The product from 3-bromo-4-hydroxy-2:5:2':5'-tetramethylbiphenylmethane having been shown to be 4:4'-dihydroxy-2:5:2':5'-tetramethylbiphenylmethane, analogous constitutions must be ascribed to the products obtained similarly from other benzyl bromides. Thus the substance, m. p. 234°, described previously as tetrabromodiphenyltetramethylstilbene (Abstr., 1896, i, 159), must be 2:5:2':5'-tetrabromo-4:4'-dihydroxy-3:6:3':6'-tetramethyldiphenylmethane, the diacetate,  $C_{24}H_{16}O_4Br_4$ , crystallises in needles, m. p. 224–225°. The constitution of this tetrabromo compound is confirmed by its reaction by means of sodium and boiling amyl alcohol to dihydroxytetramethyldiphenylmethane. The supposed bromide, m. p. 179° (Abstr., 1896, i, 422), is now found to be tribromo-*p*-xylenol.

Similarly, the substance, m. p. 232°, described previously as tetrabromodihydroxytetramethylstilbene (Abstr., 1899, i, 351), must be 2:6:2':6'-tetrabromo-4:4'-dihydroxy-3:5:3':5'-tetramethyldiphenylmethane.

The conditions under which derivatives of dihydroxydiphenylmethane are formed from hydroxybenzyl bromides and their transformation products, and the mechanism of the reactions concerned, are discussed. The following new details are given.

Whilst the action of water or alkalis on 4-hydroxy-3-allylbenzyl bromide leads to the formation of hydroxymethylbenzyl aldehyde, 4:4'-dihydroxy-3:3'-dialdehyldiphenylmethane,



m. p. 140°, was obtained on one occasion by long exposure to moist air of the residue from the preparation of the bromide.

2:2'-Dihydroxy-3:5:6:3':5':6'-hexamethyldiphenylmethane, m. p. 170° (Zancke and Horst, this vol., i, 614), is formed when trimethylsilberin is boiled with slightly acidified water.

The product, m. p. 183–184°, obtained on treating dihydroxy-4-cumenol with sodium amalgam in alkaline solution (Auer and Baum, Abstr., 1897, i, 34), is found to be 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane.

It is readily decomposed by acids or water, dipiperidylmethane and other bases remain unchanged when boiled with anhydrous sodium acetate in toluene. When heated with carbon disulphide it yields a pyridine derivative of 3:6-dibromo-4-hydroxy-2:5:

methyl-

$\text{C}_6\text{H}_4(\text{CH}_2)_2\text{C}_6\text{H}_4\text{OH}$ ,  $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_3$ .

with crystalline in strongly refracting prisms, m. p. 160—161°. Heated with ether at 100° and then shaken with carbon disulphide, the persidine derivative yields 3:6:3:6-tetrabromo-4:4'-dihydroxy-2:2':5:5'-tetramethyldiphenylmethane and the additive compound of carbon disulphide and dipiperidylmethane, m. p. 58°.

#### Reaction of Dihydroxydiphenylmethanes on Bromination

With Acetone and ERICH RIETZ (*Annalen*, 1907, 356, 152—177).

When dihydroxybenzyl bromides readily form the corresponding dihydroxydiphenylmethanes, these tend to decompose into simple benzene derivatives. The two reactions in question differ in that whereas the first is general, the second has been found to take place chiefly only in the case of certain derivatives of dihydroxydiphenylmethane. This paper is a study of the relation of the constitution of dihydroxydiphenylmethanes to their stability on bromination. It is found that, other things being equal, the stability diminishes as the number of methyl groups in the benzene nuclei increases. Thus, on careful bromination (avoidance of an excess of bromine and dilution with a solvent), the carbon chain of 4:4'-dihydroxydiphenylmethane and its dimethyl derivative remains unbroken, whilst that of the dimethyl derivative is ruptured to the extent of 2%, and that of the tetramethyl derivative to the extent of 16%. Energetic bromination of the more highly methylated derivatives leads to almost complete rupture of the carbon chain. On the other hand no decomposition takes place when 3:3'-dihydroxydiphenylmethane and its dimethyl derivative are brominated.

It is seen that the rupture of the carbon chain results from the action of the nascent hydrogen bromide; the chain remains intact on bromination in presence of sodium acetate or on treatment of the dihydroxydiphenylmethane with a solution of hydrogen bromide. The following details are new.

4:4'-Dihydroxy-3-methyldiphenylmethane,  $\text{C}_{15}\text{H}_{13}\text{O}_2$ , prepared by the method (*Ann.*, Marburg, 1901), has m. p. 133°.

The action of boiling aqueous sodium hydroxide on the condensation product of 3:5-dibromo-4-hydroxy-2:6-dimethylbenzyl bromide with pyridine or diethylamine leads to the formation of a small amount of a yellowish-brown powder,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_2$ , m. p. 173—175°. Attempts to prepare 4:4'-dihydroxy-2:6:2':6'-tetramethyldiphenylmethane from the corresponding 4:4'-diamino compound,  $\text{C}_{14}\text{H}_{22}\text{N}_2$ , m. p. 205—207°, were unsuccessful.

3:3'-Dihydroxydiphenylmethane,  $\text{C}_{12}\text{H}_8\text{O}_2$ , prepared from the 3:3'-diamino compound, crystallises in needles, m. p. 108°; the diacetate,  $\text{C}_{14}\text{H}_{10}\text{O}_4$ , crystallises in white needles, m. p. 57.5—58.5°.

3:3'-Dihydroxy-2:2'-dimethyldiphenylmethane, prepared from the 3:3'-diamino compound, forms white crystals, m. p. 159—160°.

5:5'-Dinitro-2:3:2':3'-tetramethyl- and 5:5'-dinitro-2:4:2':4'-tetramethyldiphenylmethanes,  $\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}_2$ , are obtained as light yellow powders, m. p. 164—167° and 173—176° respectively. Heated with

The following products are obtained on bromination of the corresponding dihydroxydiphenylmethanes.

**3:5:3':5'-Tetrabromo-4:4'-dihydroxydiphenylmethane**,  $m. p. 226-227^\circ$ , from 4:4'-dihydroxydiphenylmethane. **5:5':5:2'-Tetrabromo-4:4'-dihydroxy-3-methylidiphenylmethane**,  $m. p. 185-195^\circ$ , together with traces of a substance,  $m. p. 42-92^\circ$ , which may be a mixture of dibromo-*o*-cresol and tribromophenol, from 4:4'-dihydroxy-3-methylidiphenylmethane. **5:5'-Dibromo-4:4'-dihydroxydi-*m*-tolylmethane**,  $m. p. 173^\circ$ , and dibromo-*o*-cresol from 4:4'-dihydroxydi-*m*-tolylmethane. **3:3'-Dibromo-1:1'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane**,  $m. p. 172^\circ$ , and dibromo-*p*-xyleneol,  $m. p. 79-80^\circ$ , from 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane. **Dibromo-*o*-cresol**,  $m. p. 83-85^\circ$ , from 4:4'-dihydroxy-3:5:3':5'-tetramethyldiphenylmethane. A mixture of tetra- and hexabromo-derivatives from 3:3'-dihydroxydiphenylmethane. The pure **hexabromo-derivative**,  $C_{12}H_2O_6Br_6$ ,  $m. p. 241-244^\circ$ , is formed by the action of an excess of undiluted bromine; the **diacetate**,  $C_{12}H_2O_6Br_6$ , crystallizes in needles,  $m. p. 224^\circ$ . **4:6:4':6'-Tetrabromo-5:5'-dihydroxy-2:2'-dimethylidiphenylmethane**,  $C_{12}H_2O_6Br_4$ ,  $m. p. 227-228^\circ$ , from 5:5'-dihydroxydi-*o*-tolylmethane.

#### Preparation of 1:3 Dimethylpyrogallol Carbamate. (FABR.)

CHEMISCHE FABRIK (D.R. P. 181593).—1:3 Dimethylpyrogallol carbamate,  $C_6H_2(OCH_3)_2COONH_2$ , white needles,  $m. p. 148-149^\circ$ , has a beneficent action in tuberculosis which is greater than that of 1:3-dimethylpyrogallol. The latter is probably owing to the fact that it is **lactogenic**, whereas the carbamate is only gradually hydrolyzed so that a sustained reaction is rendered possible. The carbamate is prepared by the interaction of 1:3 dimethylpyrogallol and carbonyl acid chloride in anhydrous ether.

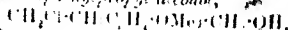
(G. T. M.)

#### Preparation of Substituted Chlorohydrins. (J. D. FABR.)

AKTIEN GESELLSCHAFT (D.R. P. 183361). When epichlorohydrin is subjected to the action of the magnesium derivatives of the aromatic halides, the condensation takes the normal course, and substituted chlorohydrins,  $CH_2ClCH(R)CH_2OH$ , are obtained, where R is an aryl or arylalkyl group.

**$\gamma$ -Chloro  $\beta$ -phenylpropyl alcohol**,  $CH_2ClCH(Ph)CH_2OH$ ,  $b. p. 153-154/28$  mm., results from the interaction of epichlorohydrin and magnesium phenyl bromide; it is, however, accompanied by  $\alpha$ -chloro bromopropyl alcohol and phenylchloropropylene.

**$\gamma$ -Chloro  $\beta$ -*p*-methoxyphenylpropyl alcohol**,



$b. p. 188-189/25$  mm., is the chief product of the interaction of magnesium *p*-methoxyphenyl bromide and epichlorohydrin.  **$\gamma$ -Chloro  $\beta$ -phenylpropyl alcohol**,  $C_6H_5CH_2CH(Cl)CH_2OH$ ,  $b. p. 153-154^\circ$ , is obtained when magnesium benzyl chloride is employed.

**Cholesterol.** **THE TRANSFORMATION OF CHOLESTANE.** **JOHNS MITCHELL (London).** 1907, 28, 1113—1124. Compare Abstr. 1906, i, 579 (63).—In view of the near relation of the cholesterol group to the terpenes, it appeared probable that, on addition of hydrogen chloride to cholesterol, cholesteryl chloride, and cholestene, a change might take place similar to that of pinene into camphene. This is now found to be the case with cholestene; on loss of hydrogen chloride, cholestene hydrochloride (chlorcholestane) yields a hydrocarbon different from cholestene and termed by the author  $\gamma$ -cholestane.

$\gamma$ -Cholestane, formed by the action of hydrogen chloride on cholestene, is obtained in two isomeric modifications, one of which crystallises in rhombic prisms, m. p. 96–97,  $[\alpha]_D^{25} + 1.7$ , and is the chief product of the reaction. The other crystallises in flat needles, m. p. 100, and is melted above 80°. Both isomeres yield the same cholestene.

$\gamma$ -Cholestene,  $C_{27}H_{48}$ , formed by boiling chlorcholestene with sodium methoxide and potassium acetate, or by treatment of the chloro-compound with zinc dust and glacial acetic acid or alcoholic silver nitrate, crystallises in flat needles, m. p. 78–79,  $[\alpha]_D^{25} + 64.86$ , and gives the same reactions of cholestene. The dibromide,  $C_{27}H_{46}Br_2$ , prepared by adding bromine dissolved in glacial acetic acid to the hydrocarbon in ethereal solution, crystallises in colourless, flat needles, m. p. 116–117, and has  $[\alpha]_D^{25} + 38.7$  immediately after solution in chloroform,  $[\alpha]_D^{25} + 36.0$  after three hours, and  $[\alpha]_D^{25} + 83.4$  after two days, the solution becoming gradually reddish yellow or dark green with slight red fluorescence, or in benzene immediately after solution  $[\alpha]_D^{25} + 88.9$ , after twenty-four hours  $[\alpha]_D^{25} + 47.0$ , and after forty-two days  $[\alpha]_D^{25} + 46.9$ , the solution remaining colourless. The saturation is probably connected with a *cis-trans* transformation; the initial fall in the rotatory power may result from the dissociation of molecular aggregates.

G. Y.

**Phytosterol.** **ADOLF WINDAUS and A. HAUER (Ber.).** 1907, 40, 1641–1650.—A convenient method of separating stigmasterol from phytosterol is described, and a direct comparison of stigmasterol and the phytosterol so obtained confirms completely the statement that they are identical (compare this vol., i, 129).

A comparison of the behaviour of cholesterol and phytosterol towards several reagents has been made. *Dihydrophytosterol*,  $C_{27}H_{48}O$ , prepared by reducing phytosterol with sodium and amyl alcohol, crystallises from acetone in stout needles or rectangular plates, m. p. 175°. The substance does not give the Selkowski colour reaction. Although the substance behaves towards bromine as an unsaturated compound, repeated reduction with sodium and amyl alcohol does not alter the melting point, and therefore the substance must be regarded as a chemical entity. A molecular weight determination of the acetyl derivative shows it to correspond with  $C_{27}H_{48}O$ . *Dihydrophytosterol acetate*,  $C_{29}H_{50}O_2$ , forms long, glistening prisms, m. p. 114–115; white reduction with sodium and amyl alcohol, it yields *dihydro- $\alpha$ -chloro- $\gamma$ -cholestane*,  $C_{27}H_{48}$ , which crystallises in rectangular leaflets, m. p. 84, heated with

This stage is only undergoing isomeric change, having been prepared by of pure amyloxyde, or, if reduction has taken place, then phytosterol must contain at least two ethylene linkings. However, on treating phytosterol with sodium amyloxyde, there was obtained, not the dihydrophytosterol, but a  $\phi$ -phytosterol,  $C_{27}H_{48}O$ , which crystallises in aggregates of needles, m. p. 146—147°. It is indifferent to sodium and amyloxy alcohol, but it is unsaturated towards bromine, the addition taking place more slowly than with phytosterol. The conclusion is drawn that dihydrophytosterol is a reduction product, and that phytosterol must contain two ethylene linkings, notwithstanding that only 1 mol. of bromine is absorbed.

Whereas cholesterol yields the same saturated substance with sodium amyloxyde, or sodium and amyloxy alcohol, it is probable that phytosterol is a reduction product, but one due to isomeric change; phytosterol, however, gives rise to two different products with these reagents (compare this vol., i, 610).

**Migration of the Phenyl Group of Aromatic Iodohydrins and Elimination of Hydrogen and Iodine from the Same Carbon Atom.** MABT. TIFFENEAU (*Compt. rend.*, 1907, 145, 93—536. Compare this vol., i, 39).—The author has previously proposed to explain the transformation of aromatic iodohydrins of the type  $OH-CArR-CHIR$  into aldehydes or ketones, when dehydrated by hydrogen iodide, by (1) loss of hydrogen and iodine from the same carbon atom and migration of the aromatic group, followed by (2) isomeric change of the vinyl alcohol derivative at first produced, thus



Study of the ethers of these iodohydrins affords experimental proof of the correctness of this view. Whilst the ethers of the aromatic iodohydrins react with silver nitrate, giving the aldehyde or ketone directly owing to hydrolysis of the vinyl derivative by the liberated nitric acid, by using mercuric oxide the reaction can be stopped at the end of the first stage. When an ethereal solution of anethole ethyl iodohydrin,  $Me-C_6H_4-CH(OEt)-CHMeI$ , is shaken with mercuric oxide, the ether  $OMe-C_6H_4-CMe(OEt)-OEt$  is formed. This has b. p. 250—251°/1044, and combines directly with bromine. Its lower homologues,  $Me-C_6H_4-CMe(OEt)-OMe$ , has b. p. 262—263° and D<sub>4</sub> 1.065, is also easily converted by acids into *p*-methoxyhydratropaldehyde.

The author considers that the iodohydrins of the type

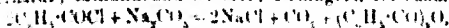


behave rather to the glycols than to the iodohydrins of the general type, since elimination of hydrogen iodide from the latter leaves a less resistant hydroxyl group, whilst elimination of HI or water from the former types leaves a more resistant hydroxyl.

**Product obtained in the Technical Preparation of Benzic Acid from Coal Tar.** GUIDO GOLDSCHMIEDT (*Moscow. Ber.*, 1901—1097).—A method of preparing benzoic acid from

and the  
Kramer  
from benzoyl chloride. The present paper is an examination of a product obtained together with the benzoyl chloride is found to consist of benzoic esters, chiefly 1:3:4-xylenyl benzoate, together with small amounts of free phenols and benzoic acid, traces of coumarone. The crude material for the preparation of benzoic acid, in spite of having been treated with alkalis, must contain 1:3:4-xylenol together with not more than traces of phenol and coumarone, which on hydrolysis of the benzonitrile esterify part of the benzoic acid.

**Hyposulphites.** IV. ARTHUR BIX and THEODOR MARX (Z. anorg. Chem., 40, 3855—3860. Compare Abstr., 1904, i, 964; 1905, i, 551; 1906, ii, 23).—Where benzoyl chloride acts on potassium azide, sodium nitrite, or sodium carbonate, it forms benzoic anhydride (Berchardt; Minunni and Calvert; Deutinger), for example:



the reactions in question taking place with great ease in the presence of pyridine. The action of benzoyl chloride on sodium hyposulphite is similar, benzoic anhydride resulting either in the presence or absence of pyridine. Three additional products are, however, obtained; from benzoyl chloride alone, benzoyl disulphide is produced; from benzoyl chloride and pyridine, in addition to benzoyl disulphide, a red base of the probable formula  $\text{C}_{11}\text{H}_7\text{N}_2\text{S}_2$ , and a yellow compound of a high molecular weight are formed.

The behaviour of benzoyl chloride towards sodium sulphite, both in the absence and presence of pyridine, has also been studied. Benzoyl disulphide is not formed in this case. The change  $2\text{C}_6\text{H}_5\cdot\text{COCl} + \text{Na}_2\text{SO}_3 = 2\text{NaCl} + (\text{C}_6\text{H}_5\cdot\text{CO})_2\text{O} + \text{SO}_2$  is accompanied by the formation of the red and yellow compounds already mentioned. The latter compounds are also formed by the action of sulphur dioxide on a mixture of benzoyl chloride and pyridine.

The yellow compound, to which the formula  $\text{C}_{11}\text{H}_7\text{O}_2\text{N}_2\text{S}_2$  is provisionally assigned, is either not dissolved by the ordinary solvents or is transformed into the red base,  $\text{C}_{11}\text{H}_7\text{N}_2\text{S}_2$ , which forms ruby-red needles, m. p. 259°. The molecular weight of the latter compound was determined by the cryoscopic method.

A. McK.

**Preparation of the Alkylamino esters of *p*-Aminobenzoic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BREUNING (D.R.P. 179627, 180221, 180292).—The esters of aromatic acids are known to possess anæsthetic properties, but only in a few cases is this action of any practical importance, owing to the circumstance that it is somewhat transient and is accompanied by irritant after-effects. It has now been found that the soluble hydrochlorides of the alkylamino esters of *p*-aminobenzoic acid produce a well-sustained anæsthesia without any disagreeable irritation.

Chloroethyl *p*-nitrobenzoate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Cl}$ , white needles, m. p. 56°, is produced by heating equal quantities of chloroethanol and *p*-nitrobenzoyl chloride at 120—125°; when heated with

piperidine is furnished. *Piperidylethyl p-aminobenzoate*, m. p. 61—62°; *piperidylethyl p-aminobenzoate*, m. p. 60°, results from the reduction of the preceding ester; its hydrochloride, m. p. 515°, crystallizes in white needles.

*Diethylaminoethyl p-nitrobenzoate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , a viscid oil, is produced by the interaction of chloroethyl p-nitrobenzoate and diethylamine. *Diethylaminoethyl p-aminonitrobenzoate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , m. p. 51°, crystallizes from dilute alcohol with  $2\text{H}_2\text{O}$ ; hydrochloride, needles, m. p. 156°.

*Diethylaminotrimethylcarbinol*,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , b. p. 70°/11 mm., obtained by the action of magnesium methyl iodide on  $\text{C}_2\text{H}_5\text{MgI}$  and aminoacetone, yields *diethylaminotrimethylcarbinyl p-nitrobenzoate*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , m. p. 47—48°, on treatment with p-nitrobenzoyl chloride. *Diethylaminotrimethylcarbinyl p-aminobenzoate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , a viscid oil, gives a crystalline hydrochloride, m. p. 183—184°. The patent contains a list of eighteen of these alkylaminoesters of p-nitrobenzoic acid with the corresponding esters of p-aminobenzoic acid and their hydrochlorides.

*Piperidylethyl p-aminobenzoate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}^+\text{H}_4$ , was obtained by dissolving hydroxyethylpiperidine and p-aminobenzoic acid in cold concentrated sulphuric acid. The solution was subsequently heated to 90—100°, poured into ice water, and rendered alkaline; the base, m. p. 56°, which is obtained from its crystalline hydrochloride, m. p. 213°, crystallizes from light petroleum in needles.

*Piperidylethyl p-dimethylaminobenzoate*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}^+\text{H}_4$ , m. p. 45°, was obtained from hydroxyethylpiperidine and p-dimethylaminobenzoic acid in benzene solution; its hydrochloride, m. p. 207°, is readily soluble in water to a neutral solution. The ester may also be prepared by heating hydroxyethylpiperidine with p-dimethylaminobenzoic acid and concentrated hydrochloric acid or by warming the base with p-dimethylaminobenzoic anhydride.

The following esters and their hydrochlorides were also prepared: *diethylaminoethyl p-diethylaminobenzoate*,  $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , oily; hydrochloride, white needles, m. p. 162—163°; *diethylaminoethyl p-aminobenzoate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ , m. p. 51°; hydrochloride, m. p. 156°; *diethylaminoethyl p-methylaminobenzoate*, oily; hydrochloride, m. p. 106—109°; *piperidylethyl p-methylaminobenzoate*, oily; hydrochloride, m. p. 145—147°; *diethylaminoethyl p-ethylaminobenzoate*, oily; hydrochloride, m. p. 119—121°.

These esters, which have important anæsthetic properties, can also be prepared by alkylating p-aminobenzoic acid or its chloride with the amino-alcohols and then reducing the products.

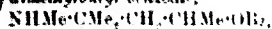
*Piperidylethyl p-aminobenzoate*, m. p. 118—119°, separates in black needles; *diethylaminoethyl p-aminobenzoate*, m. p. 82°, forms yellowish leaflets.

G. I. M.

**Preparation of Alkylaminoethyl Benzoates.** CHEMISCHES FABRIK AUF ARTIKEN, FORM. E. SCHERING (D.R.P. 181287).—The

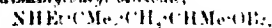
compounds having the general formula  $\text{NRE} \cdot \text{OMe} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OR}$ , where R is an alkyl group and R' either a hydrogen atom or another alkyl group. These compounds are less toxic than the amethylenes of the sartane series, and as their hydrochlorides react as neutral substances, even in concentrated solutions, they are devoid of any irritating action.

*γ-Methylamino-α,γ-dimethylbutyl benzoate.*



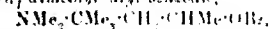
an oil substance produced by treating *γ*-methylamino-*α*,*γ*-dimethylbutyl alcohol with benzoic anhydride in the presence of water on the water bath; hydrochloride, needles, m. p. 161–162.

*γ-Ethylamino-α,γ-dimethylbutyl benzoate.*



oil prepared from *γ*-methylamino-*α*,*γ*-dimethylbutyl alcohol hydrochloride and benzyl chloride, yields a hydrochloride forming small needles, m. p. 172–173.

*γ-Isopropylamino-α,γ-dimethylbutyl benzoate.*

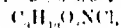


and *γ*-isobutylamino-*α*,*γ*-dimethylbutyl benzoate are oils; their hydrochlorides melt at 153–154 and 164–167 respectively.

G. T. M.

**Methyl *o*-Amino-*p*-dimethylaminobenzoate.** FRÉDÉRIC L. RICHES, *Ber.*, 1907, 40, 3686–3691; *Arch. sci. phys. nat.*, 1907, 24, 218–226; *Bull. Soc. Chim.*, [iv], 1, 295–300. It has been discovered that during the reduction of methyl nitrodimethylaminobenzoate the ester is very easily hydrolysed, and accordingly the following compounds must be deleted from the literature: Methyl-*o*-*p*-dimethylaminobenzoate hydrochloride, m. p. 228; the acetate, m. p. 232; the condensation product with chloro-*o*-nitrobenzene, m. p. 253–254; and the methyl hydroxy-*p*-dimethylaminobenzoate of m. p. 176; and its barium salt (*Abstr.*, 1906, i, 275).

The re-investigation has resulted in the preparation of 3 *acetyl*-*o*-*p*-dimethylaminobenzoic acid,  $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_2$ , which forms glistening leaflets, m. p. 246–247; the *diacetyl* compound, lamellae, m. p. 194; the *monoacetyl* compound, m. p. 193–200.



the corresponding *iodo* compound, m. p. 178–179; the corresponding *iodo* compound, m. p. 190–191, and crystallises in white needles. The *methyl* ester was obtained from the acid, and by reduction of the nitro derivative to an osmium hyposulphite in the cold; it forms prisms, m. p. 56°; the *monoacetyl* compound,  $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_2$ , has m. p. 103–104°, and the *pyruvate*, m. p. 187.

W. R.

**Naphtholmonosulphonates of Ethyl *p*-Aminobenzoate.** ANILIN-GESELLSCHAFT FOR ANILIN-FABRIKATION (D.R.P. 181324).—The naphtholmonosulphonates of ethyl *p*-aminobenzoate possess the powerful anæsthetic properties of the aminoester, and are distinguished from the salts of this substance with the mineral acids by their greater stability and solubility, and also by their neutral character. They are prepared either by the direct interaction of their





is moderately soluble in hot water, less so in the cold solvent.

G. F. M.

**p-Aminocinnamylidenecetic Acid.** HERMANN, FECHT (Ber., 1907, 40, 3891-3893. Compare following abstracts) *p-Aminocinnamylidenecetic acid* is obtained by the reduction of the  $\beta$ -acid compound by a ferrous salt in ammoniacal solution. In addition to the acid, there is produced an amorphous, dark red substance, soluble in water, which may be an abnormal ammonium salt. From *p-aminocinnamylidenemalononic acid*, the reddish yellow hydrogen ammonium salt ( $2\text{H}_2\text{O}$ ) can be prepared, the aqueous solution of which is decolorized by a few drops of acetic acid or of ammonium hydroxide. *p-Aminocinnamylidenecetic acid*, and also methyl *p-aminocinnamylidenecetate*, form dark red solutions in acetic acid or alcoholic hydrogen chloride, whereas in hydrochloric acid a yellow solution is obtained, from which red crystals of a hydrochloride are isolated; the aqueous solution is decolorized by the addition of hydroxylamine hydrochloride, with the separation of the colourless hydrochloride of an isomeric acid containing  $2\text{H}_2\text{O}$ . When the solution of this hydrochloride is boiled in the absence of excess of hydrochloric acid, the yellow, isomeric amino-acid is obtained, which is called the  $\beta$ -acid, in contradistinction to the original *p-aminocinnamylidenecetic acid*, which is called the  $\alpha$ -acid. The  $\beta$ -acid forms yellow solutions in alkalis or acetic acid, and colourless solutions in mineral acids. A hydrochloric acid solution in the cold deposits anhydrous colourless crystals of a hydrochloride, but by boiling the solution the red hydrochloride of the  $\alpha$ -acid is obtained.

The conversion of the  $\alpha$  into the  $\beta$ -acid is promoted by phenylhydrazine, aminoguanidine, or semicarbazide, as well as by hydrazine amine.

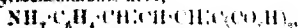
Both the  $\alpha$ - and  $\beta$ -acid give the same colourless acetyl derivative, m. p. 265° (decomp.).

**Quinone Formation. Constitution of Triphenylmethane Dyes.** HERMANN FECHT (Ber., 1907, 40, 3893-3903. Compare preceding abstracts). To the coloured salts of the *p-aminocinnamylidene* derivatives of acetic and malonic acids, the author ascribes quinonoid formulae,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}=\text{CH}\cdot\text{CH}=\text{CH}\cdot\text{CH}(\text{CO}_2\text{H})_2$ .

The carboxyl group in these acids has very little auxochromic influence. The pronounced difference in colour which exists between the salts of the two acids in alkaline solution disappears on acidification, because the group  $\text{C}=\text{C}(\text{CO}_2\text{H})_2$ , which endows the dicarboxylic acid with its deeper colour, no longer exists in the quinonoid salts which are formed in acid solution.

*α*-**Acid**,  $\text{NH}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}(\text{CO}_2\text{H})\text{CHPh}$ , m. p.  $200^\circ$  (decomp.), crystallizes from water or alcohol in yellow needles. The *β*-**acid**, m. p.  $200^\circ$  (decomp.), forms yellow crystals. They are regarded as stereoisomerides. The red *ester* of the *α*-acid has m. p.  $260^\circ$  (decomp.) and the colourless *hydrochloride* of the *β*-acid decomposes at  $250-260^\circ$ . The *esters* of the *α*- and *β*-acids, obtained by the action of diazomethane, both have m. p.  $145-146^\circ$ . The *α*-ester in benzene solution yields with absolute hydrogen chloride bluish-red needles of the *hydrochloride* of the *β*-ester, which is turned red by cold hydrochloric acid, and yields a colourless *hydrochloride* in the presence of hydroxylamine. The tertiary base,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$ , m. p.  $142^\circ$ , obtained from the *α*-ester and methyl iodide, has the same colour as the non-methylated amine and

*o*-**Acetoxycinnamylidenemalononic acid**,



m. p.  $175^\circ$ , forms orange-yellow needles and does not yield coloured salts in acid solution, the *para* isomeride, m. p.  $190^\circ$ , crystallizes in brown needles.

*o*-**Isobutylaminodiphenylethylene**,  $\text{CH}_3\text{CHPhC}_6\text{H}_4\text{NMe}_2$ , m. p.  $56^\circ$ , is obtained from *p*-dimethylaminobenzophenone and magnesium methyl iodide, the intermediately formed *carbinol*,  $\text{NMe}_2\text{C}_6\text{H}_4\text{CPhMeOH}$ , has  $\eta_{\text{sp}}/c$  2.0, 1.6 mm., and loses water at  $130^\circ$ , yielding the preceding compound. Miller's ketone and magnesium methyl iodide yield the *carbinol*,  $\text{CH}_3\text{CH}(\text{Me})\text{C}_6\text{H}_4\text{NMe}_2$ , m. p.  $152^\circ$ , which crystallizes in colourless needles and loses water on heating, forming as *tetramethylaminodiphenylethylene*,  $\text{CH}_3\text{C}(\text{Me})_2\text{C}_6\text{H}_4\text{NMe}_2$ , m. p.  $124^\circ$ , b. p.  $250-12$  mm., which, like the *carbinol*, gives a blue solution in acetic acid and yellow solutions in mineral acids.

*o*-**Acetone *p*-dimethylaminoacetophenone**,  $\text{NMe}_2\text{C}_6\text{H}_4\text{COCH}(\text{CH}_3)\text{CHPh}$ , m. p.  $150^\circ$ , prepared from cinnamantide, dimethylamine, and phosphorus oxychloride, crystallises in yellow needles, dissolves in acetic acid and mineral acids with a yellow colour, and forms a red solution with absolute hydrogen chloride. C. B.

**Sodium Salicylate**. WILHELM OCHSNER DE CONINCK (*Bull. bel. exp. Poly.*, 1907, 651--652).—When water is added, drop by drop, to a weighed quantity of sodium salicylate until this just dissolves, it is found that 1 part of the salt dissolves in 1.55 parts of water or 6.46 parts in 10 c.c. In two out of eight experiments made in the reverse way, 6.57 and 6.60 parts of the salt dissolved in 10 c.c. of water, whence it is concluded that this salt shows some tendency to form supersaturated solutions. The specific gravities of a series of solutions of sodium salicylate are given in the original. T. A. H.

**Behaviour of Very Weak Acids and Pseudo acids towards Ammonia**. ARTHUR HANTZSCH (and, in part, Miss EDITH MOWMAN and HERBERT GORKE) (*Ber.*, 1907, 40, 3798--3805).—Although simple phenols and naphthols, such as thymol, *ψ*-cuminol, mesitol, *ε*-cadinol, and *β*-naphthol, are almost completely converted into ammonium salts when exposed in an atmosphere of ammonia, those

phenols and naphthols which contain the "negative" group ortho to the hydroxyl group, such as ethyl salicylate, ethyl  $\alpha$ -naphthol-2-carboxylate, and ethyl  $\beta$ -naphthol-1-carboxylate, are practically indifferent towards ammonia at the ordinary temperature. The same retarding effect is produced by an acetyl or benzoyl group in the position ortho to the hydroxyl group. These phenols consequently belong to the group of "cryptophenols" (Auwers, *Abstr.*, 1906, 1, 838). Salol (phenyl salicylate) differs somewhat from ethyl salicylate, since it slowly absorbs ammonia to form an ammonium salt. The ammonium salt of ethyl salicylate is formed, however, when the ester is passed into a solution of the ester in light petroleum, which is at  $-16^{\circ}$ . Salicylaldehyde, ethyl *m*-hydroxybenzoate, and ethyl *p*-hydroxybenzoate absorb ammonia to form salts. Salicylaldehyde absorbs only 1 mol. of ammonia.

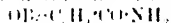
A new method for ascertaining whether a compound enters into ammonia in an indifferent solvent to form a salt is described. A known weight of the substance to be examined is dissolved in benzene and the depression of the freezing point observed, then a known quantity of ammonia in the form of a 5-10% solution in benzene is added and the depression again noted. If an ammonium salt is formed, the mol. wt. obtained from the total depression of the freezing point of the benzene will correspond with the mol. wt. of the ester. If no combination has taken place, the value obtained will be a mean of the mol. wts. of ammonia and the substance. When the observed value lies between this mean value and the mol. wt. of the ammonium salt, it denotes the partial formation of an ammonium salt.

It is stated, in conclusion, that the apparent slow precipitation of the ammonium salts of various compounds, recorded by Hantzsch and Dollfus (*Abstr.*, 1902, 1, 223) on passing ammonia into solutions of these compounds in benzene is due in some cases to super-saturation, whilst, in others, the crystals of the ammonium salt which separate out at first are so small that they can only be detected by illuminating the solution with a beam of light. The slow precipitation of an ammonium salt in benzene does not therefore indicate the presence of a pentamer.

W. H. G.

#### Acyl Derivatives of Salicylamide and Allied Compounds

KARL AUWERS (*Zee*, 1907, 40, 3596-3514). The author has pointed out previously (*Abstr.*, 1906, 1, 824) that the isomeric benzoates of salicylamide described by Titherley and Hicks (*Trans. Phil. Soc.*, 1907) are not isomeric in the sense of the formulae:



(m. p. 144, 144b) and  $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{OH} \cdot \text{NH}_2$  (m. p. 202, 202b) and that the compound with the higher melting point is the *N*-benzoate  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{Bz}$ .

The present paper is a discussion of the more recent work of McCannan and Titherley (*Trans.*, 1906, 89, 1318); the latter authors are not in agreement with the author's conclusions, and suggest that the higher melting modification exhibits tautomerism in the sense



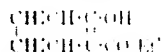
*p*-Hydroxybenzoyl O-carbamate,  $C_8H_7O_4N$ , separated from glacial acetic acid in colourless needles, m. p. 218–220°.

Determinations of the molecular weights of acetyl benzamide, *p*-acetylsalicylamide, and *O*-benzoylsalicylamide respectively in *p*-dimethylacetone solutions are submitted in support of the views advanced.

*O*-Benzoylsalicylacetamide,  $OBzC_6H_4CH_2CO-NH_2$ , obtained by acetylation of *p*-hydroxyphenylacetamide, separates from alcohol in shining leaflets, m. p. 162–164°. It is insoluble in alkali and is converted by cold concentrated sulphuric acid into the original compound and is accordingly an *O*-ester. The constitution was proved and further by conversion of the compound into *o*-benzoylsalicylacetamide,  $C_8H_7O_4N$ , by means of phosphoric oxide, the latter compound separates from light petroleum in needles, m. p. 50°, and, when agitated, forms *o*-hydroxybenzyl cyanide, which separates from a mixture of light petroleum and benzene in colourless needles, m. p. 117–118°. A. McK.

**Phenylhydrazone of Salicylic Acid.** HUGO SCHROETER and LEON FRIEDMAN *Monatsh.*, 1907, 28, 1092–1100. Compare Madsen, *ibid.*, 4, 423. The resemblance of the enolic formula of ethyl

acetoacetate,  $\begin{smallmatrix} CH_3COH \\ | \\ CH-CO-Et \end{smallmatrix}$ , to the formula of ethyl salicylate,



suggested that the latter or its ketonic form should undergo condensations similar to those of ethyl acetoacetate. This view has led the authors to investigate the action of phenylhydrazine on methyl salicylate.

When heated with 2 mols. of freshly distilled phenylhydrazine and a few drops of piperidine in a reflux apparatus on a water bath, methyl salicylate forms *salicylic acid phenylbenzoyl azo*,  $C_{17}H_{15}O_2N_2$ , in 40% yield. This crystallises in white leaflets, m. p. 130°, gives a violet coloration when heated with aqueous, or in the cold with aqueous alcoholic, ferric chloride, reduces ammoniacal silver, platinum

$\begin{smallmatrix} N-SHPh \\ | \\ H \\ | \\ CO-H \end{smallmatrix}$  chloride, and Fehling's solution, dissolves in aqueous alkali carbonates, and can be recrystallised from concentrated sulphuric acid. It must have the annexed constitution. The ammonium salt exists

in solution; the potassium, sodium, calcium, and barium salts readily decompose on recrystallisation or on evaporation of their aqueous solutions. The piperidine salt,  $C_{17}H_{15}O_2N_2 \cdot C_4H_9N$ , is obtained in 30% yield by heating methyl salicylate and phenylhydrazine with an excess of piperidine; it crystallises in nacreous leaflets, m. p. 157°, is neutral in cold, but alkaline in hot aqueous solution, and is decomposed slowly at 100° or by prolonged action of steam, or more quickly by aqueous alkalis. G. Y.

**Synthesis of Iodogorgonic Acid.** HENRY L. WHEELER (*Am. Chem. J.*, 1907, 33, 356–358). Henze (*ibid.*, vol. 1, 370) has referred to the iodogorgonic acid prepared by Wheeler and Jamieson (*Abstr.*,

... acid, was really the inactive variety, and that the iodotyrosine (di-iodotyrosine) produced was also inactive and identical in every respect with the natural acid.

**m-Hydroxytritanolactone.** HAYS VON LINSIG and PAUL KURY (*J. pr. Chem.*, 1907, [ii], 76, 275-277. Compare *Abstr.*, 1908, 1, 781; this vol., i, 45). The condensation of benzil with formaldehyde in presence of zinc chloride leads to the formation of a substance crystallising in colourless needles, m. p. 239°, and *m*-hydroxytritanolactone,  $C_{20}H_{14}O_2$ , which crystallises in rhombic leaflets, m. p. 124°. The sodium,  $C_{20}H_{13}O_2Na$ , disodium,  $C_{20}H_{12}O_2Na_2$ , potassium, and ammonium salts have been analysed. Whilst *m*-hydroxytritanolactone remains unchanged on evaporation of its solutions, the alkali salts, on heating, form diphenylmethane. *Bromo-m-hydroxytritanolactone*,  $C_{20}H_{13}BrO_2$ , forms colourless, rhombic leaflets, m. p. 129°.

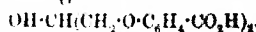
*m*-Methoxytritanic acid,  $C_{21}H_{18}O_5$ , prepared by hydrolysis of the methyl ester, crystallises in rhombic leaflets, m. p. 237°, and loses carbon dioxide at about 280°. The potassium salt,  $C_{21}H_{17}O_5K$ , crystallises in needles. The methyl ester,  $C_{22}H_{20}O_5$ , forms stout prisms, m. p. 154°.

*m*-Ethoxytritanic acid,  $C_{22}H_{20}O_5$ , crystallises in needles, m. p. 154°, boils slightly above its m. p. in a vacuum, and loses carbon dioxide when heated under atmospheric pressure. The potassium salt,  $C_{22}H_{19}O_5K$ , was analysed. The ethyl ester,  $C_{24}H_{22}O_5$ , forms rhombic prisms, m. p. 84°.

*m*-Methoxytritanol,  $C_{20}H_{18}O_4$ , prepared by the action of concentrated sulphuric acid or of lead dioxide and glacial acetic acid on *m*-methoxytritanic acid, remains unchanged when heated at 350° or when boiled with ethereal or alcoholic hydrogen chloride. *m*-Methoxytritanol,  $C_{20}H_{18}O_4$ , formed by heating *m*-methoxytritanic acid, separates from alcohol in small, rhombic crystals, m. p. 116°. *m*-Ethoxytritanol crystallises in large prisms, m. p. 68°. *m*-Hydroxytritanol,  $C_{20}H_{18}O_4$ , formed by heating the methyl ether or methoxytritanol or ethoxytritanol with hydrogen iodide and glacial acetic acid, crystallises in rhombic leaflets, m. p. 124°. These tritanic acids and tritanol derivatives give a violet coloration with concentrated sulphuric acid, the tritanic derivatives give a yellow coloration. Only *m*-hydroxytritanol solution does not give a coloration.

**The Condensation of Salicylic Acid with Epichlorohydrin or the Dichlorohydrins.** MARTIN LANGE (D.R.P. 181,001: "Salicylic acid," when condensed in sodium hydroxide solution with epichlorohydrin or  $\alpha$ - or  $\beta$ -dichlorohydrin, gives rise to the soluble sodium salt of a condensation product which corresponds with either

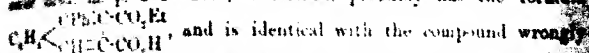
of the following formulae:  $\begin{matrix} \text{CH} \\ | \\ \text{O} \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$  or



The free acid, m. p. 167°, crystallises from dilute alcohol in aggregates

of stibic acid  
or alkalis.

**Polymerisation of Ethyl Phenylpropiolate.** PAUL FRIEDMAN and W. MOLLER (*Rev.*, 1907, 40, 3839—3844. Compare Stobbe, *loc. cit.*, i, 769).—Ethyl phenylpropiolate is converted when heated in sealed tube at 210° for ten to twelve hours into *diethyl 1-phenyl-2:3-dicarboxylate*, m. p. 127—128°, identical with the compound described wrongly by Lanzer as triethyl triphenyltrimaleate (Abstr., 1909, i, 916). Only one of the carboxy groups is hydrolysed by an aqueous or alcoholic solution of potassium hydroxide; the ester acid, m. p. 202—203°, so formed, probably has the formula



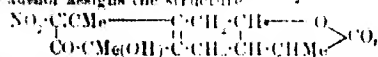
described by Lanzer and Halverson (Abstr., 1902, i, 458) as monoethyl diphenylmethenecarboxylate. It crystallises with 4H<sub>2</sub>O, which are driven off on heating the substance; the sodium salt, C<sub>20</sub>H<sub>15</sub>O<sub>4</sub>Na, 6H<sub>2</sub>O, crystallises in small, silvery leaflets; the calcium salt, (C<sub>20</sub>H<sub>15</sub>O<sub>4</sub>)Ca, forms small, slender needles; the pyridinium salt, C<sub>20</sub>H<sub>15</sub>O<sub>4</sub>C<sub>5</sub>H<sub>5</sub>NH, forms brilliant, quadratic plates, m. p. 150—152°. A mixture of the sodium salt and calcium hydroxide yields, on distillation at 325°, a substance which crystallises in brilliant, brownish-yellow needles, m. p. 157°, and is probably *allochrysoketone* (compare Stobbe, this vol., i, 765).

W. H. G.

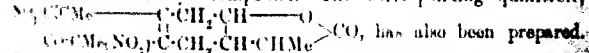
**ψ Quinol Derivatives of the Santonin Group.** GENIO BAKKUSSEN (*Ann. R. Acad. Lincei*, 1907, [8], 16, n, 262—265).—Since the desmotroposantonins and the santonous acids contain the same ring,

$\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_3$ , as is present in 1:4 dimethyl β naphthol, the author

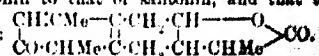
has investigated the oxidation of these compounds to ascertain if they also yield derivatives of the ψ quinol type (compare this vol., i, 914). Desmotroposantonous acid gives a ψ quinol which is apparently isomeric with santoninic acid and yields an azo compound when treated with phenylhydrazine. From desmotroposantonin has been prepared, not the corresponding ψ quinol or hydroxysantonin, but its nitro-derivative which was obtained by Androschi (Abstr., 1898, i, 266), and to which the author assigns the structure



as it forms an acetyl compound. The corresponding quintitrole,



The capacity of the aromatic ring of desmotroposantonin and desmotroposantonous acid of becoming alicyclic in the transformation of these compounds into ψ quinols would indicate that the type changes from that of desmotroposantonin to that of santonin, and that the latter should have the formula:



T. H. P.

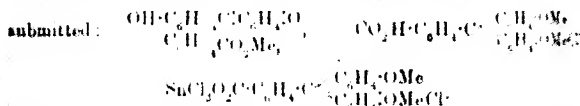
**Constitution of Phenolphthalein.** KURT H. MEYER and KARL MAX (*Ber.*, 1907, 40, 3603-3605).—An intensely yellow *lactoid* quinonoid derivative of phenolphthalein, m. p. 98-104°, similar to the quinonoid derivative of tetrabromophenolphthalein (this vol., p. 421), has been prepared by the action of ethyl iodide on the solid potassium salt; on recrystallization, it is transformed into the stable lactone ether, m. p. 118-120°.

The absorption spectra of the alkali salts of phenolphthalein, quinolphthalein, and fluorescein are compared. If the wavelengths of the absorbed light are taken as a function of the concentration of the solutions, the three spectra give similar curves. That the curve for fluorescein, although differing in position, is similar in shape to those for phenolphthalein and quinolphthalein, when these curves are taken together, shows that the difference between these three substances is one of degree and not fundamental. G. Y.

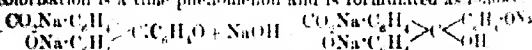
#### Halochromism of Phenolphthalein and its Esters. KURT H. MEYER and ARTHUR HANTZSCH (*Ber.*, 1907, 40, 3470-3482).

Whilst the behaviour of phenolphthalein towards alkalis and the constitution of its alkali salts have been frequently investigated, its basic properties and its power of forming salts with acids have been comparatively little studied. The authors have accordingly found that phenolphthalein forms a red salt with hydrogen chloride at 0°, but the salt could not be isolated; on the other hand, bromate red compounds were obtained with aluminium chloride and stannic chloride respectively. The lactoid dimethyl ether of phenolphthalein exhibits a similar behaviour towards these chlorides.

The authors confirm the results of Green and King (*Natr.*, 1906, p. 670) with regard to the quinonoid methyl ester of phenolphthalein and agree with their theoretical conclusions. This compound also forms double salts. Since the alkali salts of phenolphthalein have the same colour as those of the quinonoid ester, the quinonoid formula is assigned to the former. The following formulae are accordingly



The fact that the red colour of phenolphthalein in alkaline solution is discharged by excess of alkali is not due to the formation of the colourless sodium salt of phenolphthalein, as is often supposed; the decolorisation is a time phenomenon and is formulated as follows:

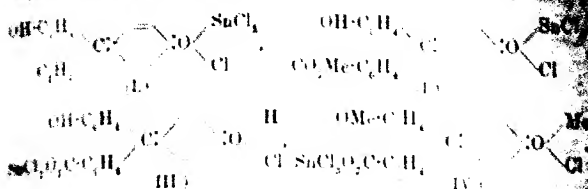


The quinonoid monomethyl ester of phenolphthalein also formed double salts with stannic chloride and aluminium chloride; these salts are undoubtedly of quinonoid structure.

The double salts of phenolphthalein and its lactoid dimethyl ether have, not only the same colour when solid, namely, cinnabar red, but in solution have almost the same absorption spectra as the salts of the

draws that the salts of the lactoid ether are quinonoid. The fact, as well as phenolphthalein with acids are quinonoid.

The tin double salts of benzaurin (I), the quinonoid ester (II), phenolphthalein (III), and the lactoid dimethyl ether (IV) are respectively represented as follows:



When hydrogen chloride is passed over dry phenolphthalein at the ordinary temperature, there is no change, but at  $-30^{\circ}$  addition of from 1 to 2 mols. of the acid takes place, the salt being red; on rise of temperature, however, all the hydrogen chloride is eliminated.

The salt,  $C_{20}H_{14}O_6 \cdot AlCl_3$ , obtained by adding the calculated amount of a solution of aluminium chloride in nitrobenzene to a solution of phenolphthalein in nitrobenzene and then pouring the mixture into carbon disulphide, is a cinnabar red powder, which chars on being heated. The salt,  $C_{20}H_{14}O_6 \cdot C_6H_5 \cdot NO_2 \cdot SnCl_4$ , obtained from stannous chloride in a similar manner, is a red, hygroscopic powder. The salt,  $C_{20}H_{14}O_6 \cdot AlCl_3$ , obtained from the lactoid dimethyl ether, is a cinnabar red powder. The salt,  $C_{22}H_{16}O_6 \cdot SnCl_4$ , forms red crystals, m. p.  $128-129^{\circ}$ ; its solution in chloroform is red, its alcoholic solution orange-yellow.

Quinonoid phenolphthalein methyl ester (methyl benzaurin-carboxylate), obtained by the action of methyl sulphate on phenolphthalein (compare Green and King, *loc. cit.*), is a red, amorphous powder melting indefinitely between  $127^{\circ}$  and  $136^{\circ}$ . Its concentrated solutions are red, but become yellow on dilution; its solution in liquid ammonia is reddish violet. It undergoes saponification with great ease; it forms the salt,  $C_{21}H_{16}O_6 \cdot AlCl_3$ , which is a cinnabar red powder. The salt,  $C_{21}H_{16}O_6 \cdot SnCl_4$ , forms red flakes.

The absorption spectra of the tin double salts prepared are described.

The red solutions of phenolphthalein alkali salts require such a large excess of alkali in order to be decolorised that the reaction cannot be clearly followed by conductivity measurements. Tetrabromophenolphthalein was, however, examined from this standpoint. A. McK.

#### Constitution of the Phenolphthalein and Quinolphenthalein

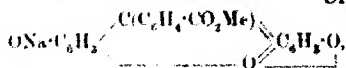
Salts II. ARTHUR G. GREEN and PERRY E. KING (*Ber.*, 1907, 40, 3724-3734. Compare Abstr., 1906, i, 670\*.)—The scarlet compound described previously as the quinonoid methyl ester of phenolphthalein is found to be the hydrochloride of the ester. The ester, which is much

\* See also *Proc.*, 1907, 23, 228.

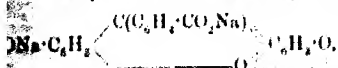


...drying dry  
...ethyl alcohol  
...into ammonium hydride at 0°. After purification, it crystallises  
orange, prismatic needles, and in alcoholic solution yields with hydro-  
chloric acid a scarlet solution of the chloride which gradually loses its  
colour and yields phenolphthalein. The ester forms a violet-red solu-  
tion in alkali hydroxides, from which the unchanged methyl ester is  
obtained by immediate acidification and phenolphthalein by subsequent  
acidification. The methyl ester of quinolphthalein in the form of its  
chloride exhibits precisely analogous behaviour, and forms a black  
purple solution in alkalis.

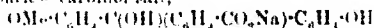
For these coloured alkali salts of the esters, the authors suggested  
the formula:  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}) : \text{C}_6\text{H}_4 \cdot \text{O} < \text{OH}$  and



and from analogy the coloured salts of phenol- and of quinolphthaleins  
must be represented by  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Na}) : \text{C}_6\text{H}_4 \cdot \text{O} < \text{OH}$  and

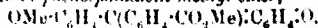


These conclusions, which accord with the behaviour of the salts of  
the phthalic acids and their esters with excess of potassium hydroxide and  
with alcohol, the salts of the esters remaining coloured, are confirmed  
by a study of the lactonoid methyl and dimethyl ethers of phenol-  
phthalein and quinolphthalein (Meyer and Spengler, *Monatsh.* 19-2,  
p. 440). The methyl ethers represented by the preceding structural  
formulas would not contain a phenolic hydroxyl group, and con-  
sequently should not form coloured alkali salts, and should yield esters  
insoluble in alkalis. This is actually the case. Phenolphthalein  
methyl ether has a double m. p. initially at 148-149°, and after  
remolodification at 80°; in alkalis, it yields a faintly red solution, the  
colour of which is weaker the purer the ether (Meyer and Spengler  
ibid. p. 141-142; red solution in alkalis). This solution probably con-  
tains the colourless carbinol salt,



Quinolphthalein methyl ether separates from benzene in solution  
prisms, m. p. 118-122°, and after removal of the benzene of crystal-  
lisation, m. p. 107-109°; it dissolves in alkalis forming a colourless  
solution of the carbinol salt (compare Nietzki and Burckhardt, *Abstr.*  
1917, i, 225).

The methyl ester of phenolphthalein methyl ether,



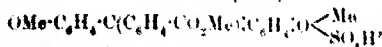
obtained from the lactonoid methyl ether in a similar manner to the  
methyl ester of phenolphthalein, is an orange substance insoluble in  
alkalis; the hydrolysed compound yields the original lactonoid ether  
by acidification. The methyl ester of quinolphthalein methyl ether is  
obtained in the form of the chloride,

when dry hydrogen chloride is passed into a solution of the lactonid ether; it forms red plates, readily lones methyl is insoluble in aqueous alkalis, and yields the lactonid.

**Hydrolysis.** The *chloride*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \text{OCl}$

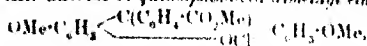
is prepared by passing hydrogen chloride into a glacial acetic solution of quinolphthalein methyl ether; it forms dark red, glassy crystals, and is instantaneously decomposed by water or moist air.

The esters of dimethylated phenol or quinolphthalein are obtained only in the form of salts, such as the *sulphate*,



which is an unstable, scarlet substance. More stable is the red double salt,  $2 \cdot \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me})_2 \text{O} \cdot \text{C}_6\text{H}_5 \cdot \text{OMe} \cdot \text{Cl} \cdot \text{SnOCl}_2$ , which does not decompose by water, alcohol, or alkalis with regeneration of the quinolphthalein.

The *acetyl ester chloride of quinolphthalein dimethyl ether*,



is isolated in the form of the double salt,  $2 \cdot \text{C}_{22}\text{H}_{19}\text{O}_4\text{Cl} \cdot \text{ZnCl}_2$ , which is a orange red substance.

**Preparation of *o*-Carboxyphenylthioglycollic Acid.** KATZ & CO. (D.R.P. 181658).—When diazotised anthranilic acid is treated with sodium monosulphide, a poor yield of thiosalicylic acid is obtained, but when sodium poly-sulphide is employed a new sulphur derivative is obtained, which, unlike thiosalicylic acid, is insoluble in alcohol, and yields *o*-carboxyphenylthioglycollic acid,  $\text{C}_6\text{H}_4(\text{H}) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , on treatment with an alkaline solution of sodium chloroacetate.

G. T. M.

**Nitration of Benzoylvanillin.** JOAN PEROVICI (*Ber.*, 1907, 35, 1504—1506).—When benzoylvanillin is nitrated by cold concentrated nitric acid, one nitro-group only enters into the ring. It takes up the ortho-position relatively to the aldehyde group; this was proved by comparing the compound obtained with that resulting from the action of benzoyl chloride on (vic.) *o*-nitrovanillin; the phenylhydrazones are also identical.

*Benzoylvanillinphenylhydrazone* separates from glacial acetic acid in prisms, m. p. 209—210° (corr.).

*vic.* *o*-Nitrobenzoylvanillin,  $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{NO}_2)(\text{OMe}) \cdot \text{OBz}$  (1:2:5:4), separates from glacial acetic in colourless prisms, m. p. 97°. Its *phenylhydrazone* separates from glacial acetic acid in golden-yellow plates, m. p. 192°.

A. McK.

**cyclo-Butanone.** NICHOLAI M. KILNER (*J. Russ. Phys. Chem. Soc.*, 1907, 30, 922—925. Compare Abstr., 1905, i, 355).—Further details are given for the preparation of pure cyclobutanone together with fresh determinations of some physical constants. *cyclo*-Butanone, b. p. 98.5—99°/765 mm.;  $D_4^{20}$  0.9548;  $D_4^{25}$  0.9382;  $n_D^{20}$  1.4230. The

...oxide and water, 1:1, ... into ...  
 cyclobutanone and an unsaturated bromide, probably  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-$ ,  
 b. p. 93—95°.

**cycloNonanone.** RICHARD WILLSTÄTTER and TOKUHEI KANE-  
 YAKI (*Ber.*, 1907, 40, 3875).—The authors confirm the observations of  
 Zelinsky (this vol., i, 780) regarding the formation of cyclo-nonanone  
 from sebatic acid.

**Terpenes and Etheral Oils. LXXXVII. Nopinone.** ...  
 WALLACH and ARNOLD BLEMMANN (*Annalen*, 1907, 356, 227).—  
 Nopinone (Bayer and Villiger, Abstr., 1896, i, 622) has been  
 prepared previously in such small amounts that only its b. p. has  
 been determined. It was desirable therefore to attempt the pre-  
 paration of larger quantities.

Nopic acid, m. p. 126°,  $[\alpha]_D^{20} = -15.64$ , is best isolated from the  
 oxidation product of turpentine oil by conversion into its sparingly  
 soluble sodium salt. Much better yields are obtained from native  
 rotatory American than from levorotatory French turpentine oil.

Nopinone,  $\text{C}_{15}\text{H}_{24}\text{O}$ , is obtained in good yields by adding potassium  
 permanganate and concentrated sulphuric acid to a hot aqueous  
 solution of sodium nopate. It solidifies in a freezing mixture to a  
 crystalline mass, m. p. slightly above 0°, b. p. 203°, D<sub>4</sub> 0.881,  $n_D^{20} 1.475$ ,  
 $[\alpha]_D^{20} +18.48$  when undiluted,  $+37.27$  —  $+38.04$  in alcohol,  $+11.07$   
 in ether, or  $+10.79$  —  $+10.95$  in benzene. When treated with  
 hydrogen chloride in alcoholic solution, it condenses, forming the  
 trichloride,  $\text{C}_{15}\text{H}_{21}\text{OCl}_3$ , which crystallises in stout prisms, m. p.  
 148° (evolving gas), and on prolonged boiling in solution of digesting  
 with 1 mol. of sodium ethoxide is converted into the monochloride,  
 $\text{C}_{15}\text{H}_{23}\text{OCl}$ , crystallising in needles, m. p. 125—126°. The trichloride  
 is again formed on treating the dichloride with hydrogen chloride in  
 alcoholic solution; the ease with which it is formed together with its  
 sparing solubility makes the trichloride suitable for the preparation of  
 nopinone. On prolonged boiling with dilute sulphuric acid, nopinone is  
 transformed into 1-isopropyl- $\Delta^2$ -cyclohexene-4-one (Abstr., 1906, i, 125).

Reduction of nopinone with sodium in moist ethereal solution leads  
 to the formation of two nopinols, probably *cis*- and *trans*-isomers.  
 $\alpha$ -Nopinol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , sublimes in white needles, m. p. 147°  
 b. p. 204—205°,  $[\alpha]_D^{20} = -5.32$ , remains unchanged in contact with  
 dilute sulphuric acid, and forms a phenylurethane,  $\text{NHPh} \cdot \text{O} \cdot \text{C}_6\text{H}_5$ ,  
 m. p. 131—132°.  $\beta$ -Nopinol is obtained as a viscid mass, a. p. 124°  
 forms a phenylurethane, m. p. 95—96°, and when heated with conc.  
 chloride yields a small amount of nopinonene,  $\text{C}_{15}\text{H}_{22}$ , b. p. 157—158°.

Reduction of nopinone by means of sodium in alcoholic solution  
 leads to the formation of the pinene,  $\text{C}_{15}\text{H}_{20}$ , which is obtained in  
 crystals, m. p. 106—107°, b. p. 195—200°, 11 mm.

**Homopinol (methylnopinol, pinene hydrate)**,  $\text{C}_{15}\text{H}_{26}\text{O}$ , prepared  
 by the action of magnesium methyl iodide on nopinone, crystallises in  
 needles, m. p. 58—59°, b. p. 204—205°,  $[\alpha]_D^{20} = -4.99$ , has an odour  
 resembling camphor, is stable towards permanganate, and yields on

when treated with concentrated sulfuric acid. The action of sulfuric acid on homonopinol leads to the formation of a mixture of products resulting probably from the primary formation of terpin and its further transformation of this into dipentene, terpinol, terpinol and terpineol. Dipentene dihydrochloride is formed by the action of hydrogen chloride on homonopinol in glacial acetic acid solution.

When heated with zinc chloride, homonopinol yields polymerization products together with small amounts of hydrocarbons, which boil chiefly at 170–180°, are volatile with steam, and have an odour of lavender. The action of potassium hydrogen sulphate on homonopinol at 120° leads to the formation of a hydrocarbon,  $C_{10}H_{16}$ , b. p. 163–164°.

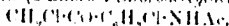
On treatment with phosphorus pentachloride in light petroleum homonopinol yields a chloride,  $C_{10}H_{15}Cl$ , b. p. 95–105°/13 mm. at 760 mm. evolving hydrogen chloride, which is isomeric with the chloride obtained by the action of hydrogen chloride on pinene and on treatment with hydrogen chloride in glacial acetic acid solution yields dipentene dihydrochloride. The action of amyl nitrite and nitric acid on the chloride leads to the formation of a nitro compound containing chlorine, when treated with aniline, the chloride yields dipentene. This chloride may be formed as an intermediate product in the formation of dipentene by the action of hydrogen chloride on monopinene.

G. Y.

[Alkylation of  $\psi$  Ionone] HAARMANN and REIMER (D.R.-P. 163,950).— $\psi$  Ionone, when mixed with five parts of methyl sulphate and the solution subsequently warmed at 40°, yields an alkylated product which is separated by distillation in steam. The alkyl derivative when freed from ionone by sodium hydrogen sulphite has the following properties: b. p. 135–142 mm.,  $d_4^{20}$  0.945,  $n_D^{20}$  1.5150. It is, however, a mixture, the ketonic constituent of which when separated by means of semicarbazone has b. p. 120–128°/12 mm.,  $d_4^{20}$  0.940,  $n_D^{20}$  1.491–1.494. A semicarbazide,  $C_{12}H_{19}ON$ , was obtained, m. p. 182–183°. These results point to the production of a new methyl ketone.

G. T. M.

1-Chloroacetyl 2 chloro 4 aminobenzene [ $\omega$ -2 Dichloro-4-aminoacetophenone] and its Derivatives. FRANZ KUNCKEL and A. RICHARTZ (Ber., 1907, 40, 3394–3397).— $\omega$ -2-Dichloro-4-aminylaminoacetophenone (3 chloro 4 chloroacetylacetanilide),

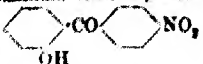


obtained by Friedel-Craft's synthesis from chloroacetyl chloride and 4-chloroacetanilide in the presence of carbon disulphide, crystallises from benzene and melts at 146–147°.

When oxidised with acidified permanganate, the ketone yields 1-chloro-2-aminobenzene acid,  $C_6H_4ClNO_2$ , m. p. 206–207°, and this on hydrolysis yields Tiemann's 2-chloro-4-aminobenzoic acid (Ber., 1891, 704).

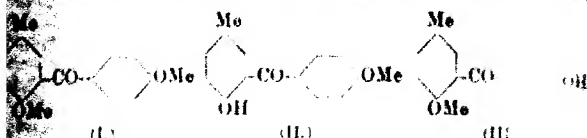
$\omega$ -2-Dichloro-4-aminylaminoacetophenone, obtained by hydrolysing the acetyl derivative, yields a hydrochloride,  $CH_3ClCO\cdot C_6H_3Cl_2\cdot NH_2\cdot HCl$ , in the form of yellowish-red needles, m. p. 278° (decomp.). The free amine melts at 95–97°.

J. J. S.

...ketones.  
3521)---It  
...pointed out by Aronow (ibid., 1937, 17) that, by the  
...phenetole with *p*-nitrobenzoyl chloride in the  
...presence of aluminium chloride, small amounts of 4'-nitro-2,4,6-tri-  
...phenone, , are formed in addition to the

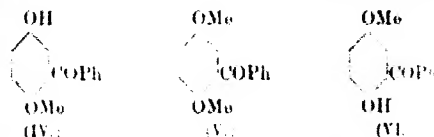
usual product, 4'-nitro-4-ethoxybenzophenone. The conclusion was  
...shown that the ethers of aromatic *o*-hydroxyketones are more readily  
...saponified than the isomeric *para*-derivatives.

In support of this view, the authors have studied the behaviour of  
...ketones (I) on saponification with aluminium chloride. A mono-



methylated compound is formed which is not attacked by aluminium  
chloride even at 220°. The other methyl group, on the other hand, is  
eliminated with remarkable ease; in the synthesis of the dimethyl ether  
from *p*-cresol methyl ether and anisic chloride, the monomethyl ether  
is formed in about the same amount of the dimethyl ether. Thus the  
product of the partial saponification has the formula (II) as proved  
by the fact that the isomeric ether (III) is produced by the saponifica-  
tion of *p*-cresol methyl ether with *p*-nitrobenzoyl chloride and sub-  
sequent displacement of the nitro- by the hydroxy-group. The latter  
compound is saponified with great ease.

Kauffmann ascribed the formula (IV) to the substance obtained



the partial saponification of the compound (V). The authors con-  
sider that the correct formula is (VI), since cryoscopic determinations  
in dibromobenzene solutions give normal values.

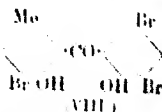
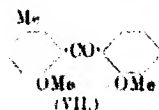
Similar results were obtained with ethers of another series of  
hydroxy-ketones.

1. 4'-Dimethoxy-5-methylbenzophenone,  $C_{16}H_{14}O_3$ , separates from ligro-  
ne in colourless needles, m. p. 69–70°. 2-Hydroxy-4-methoxy-  
benzophenone,  $C_{15}H_{12}O_3$ , separates from dilute alcohol in yellow  
leaflets, m. p. 108–109°. Its dibromo-derivative,  $C_{15}H_{10}Br_2O_3$ , crys-  
tallizes from glacial acetic acid in yellow needles, m. p. 165–167°.  
4'-Methoxy-2-methyl-5-methylbenzophenone,  $C_{15}H_{12}O_3$ , separates from  
light petroleum in golden, glistening leaflets, m. p. 101–102°.

separates from benzene in tiny needles, m. p. 137°. 4. *2-methoxy-5-methylbenzophenone*,  $C_{11}H_{12}O_2$ , separates from dilute acetic acid in tiny needles, m. p. 137°.

4. *2-Hydroxy-2-methoxy-5-methylbenzophenone*,  $C_{11}H_{12}O_3$ , obtained from 2-methoxy-5-methylbenzophenone by replacing the acetyl group by the hydroxy group, crystallises from benzene in glistening needles, m. p. 166°. When saponified, it forms 2:4-dihydroxy-5-methylbenzophenone,  $C_{11}H_{12}O_4$ , which crystallises from benzene in tiny needles, m. p. 150–151°. The latter compound forms a tribromo derivative,  $C_{11}H_7O_4Br_3$ , crystallising from glacial acetic acid in yellow needles, m. p. 211.5–202.5°.

The ketone (VII), obtained from *o*-methoxybenzoyl chloride,



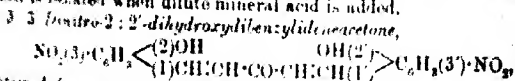
*o*-methyl ether, was saponified at 160° with aluminium chloride and the product brominated, when the tribromo compound (VIII) was obtained; it separates from glacial acetic acid in yellow crystals melting indefinitely at 190°.

A. MOK.

**Dinitro and Dibromo-2:2'-dihydroxydibenzylideneacetone**  
 EROSE FABIANY and TIBOR SZÉKÉI (*Ber.*, 1907, 40, 3435–3461).  
 Compounds of the types  $\text{CH}(\text{R})\text{CH}(\text{CO})\text{CH}(\text{R})\text{CH}$  and  $\text{CH}(\text{R})\text{CH}(\text{CO})\text{CH}(\text{R})\text{CH}$

have already been studied by Chaisen and others; the authors have been interested in the effect of the substitution of nitro- or bromo- groups on the behaviour as dyes of these types which possess the complex chromophore  $\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{O})$ , are symmetrically constituted, and in which the two hydrogen atoms in the ortho-positions in each ring are substituted by hydroxyl groups.

It has been previously shown by Fabinyi (D.R.P. 110521) that salicylaldehyde and acetone interact in alcoholic solution in the presence of concentrated sodium hydroxide to form the sodium salt of 2:2'-dihydroxydibenzylideneacetone, from which the latter compound itself is isolated when dilute mineral acid is added.



obtained from *m*-(*vic*)-nitrosalicylaldehyde in an analogous manner, separates from alcohol in yellow needles, m. p. 231–232° (decomp.). Its solution in concentrated sulphuric acid is yellowish-red and becomes ruby-red on the addition of water. The sodium salt forms glistening ruby-red crystals. The diacetyl derivative separates from glacial acetic acid in yellow crystals, m. p. 228–230° (decomp.); the dibenzoyl derivative separates from nitrobenzene in tiny, yellow crystals, m. p. 225–226° (decomp.).

**2:2-Dinitro-2:2-dihydroxydibenzylidenacetone** is obtained from 5-bromosalicylaldehyde, separates from alcohol in orange-yellow crystals, m. p. 212—214° (decomp.); its solution in concentrated sulphuric acid is orange-red; its sodium salt is reddish-brown. Its *diacetyl* derivative separates from glacial acetic acid in yellow scales, m. p. 203°.

**4:4'-Dinitro-2:2-dihydroxydibenzylidenacetone**, obtained by the direct nitration of 2:2-dihydroxydibenzylidenacetone, separates from alcohol in tiny needles, m. p. about 204° (decomp.); its solution in concentrated sulphuric acid is orange-red, its solution in dilute cherry-red; its sodium salt is dark red. Its *diacetyl* derivative separates from glacial acetic acid in tiny leaflets, m. p. 196° (decomp.).

By the action of concentrated nitric acid on 2:2-dihydroxydibenzylidenacetone, the more highly nitrated compound, *tetrakis*-(2:2-dihydroxydibenzylidenacetone),  $\text{C}_6(\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2)_2)_4\text{O}_4$ , may be obtained under the conditions quoted; it separates from nitrobenzene in yellow needles; its solution in concentrated sulphuric acid is orange-coloured; it begins to decompose at 240°.

**5:5'-Dibromo-2:2-dihydroxydibenzylidenacetone**, obtained from 5-bromosalicylaldehyde, crystallises from alcohol in yellow needles, m. p. 188° (decomp.); its solution in dilute aqueous sodium hydroxide is red, and the sodium salt is reddish-brown. Its solution in concentrated sulphuric acid is cherry-red; its solution in concentrated aqueous sodium hydroxide is bluish-violet. Its *diacetyl* derivative crystallises from glacial acetic acid in tiny, yellow needles, m. p. 187—188° (decomp.). The *dimethoxy*-derivative, obtained by the action of methyl iodide on the sodium salt, crystallises from alcohol in yellow leaflets, m. p. 137; the *diethoxy*-derivative forms yellow leaflets, m. p. 131. The *dibenzoyl* derivative crystallises from benzene in yellow crystals, m. p. 221° (decomp.).

**2:2-Diacetoxydibenzylidenacetone** crystallises from glacial acetic acid or alcohol in yellow needles, m. p. 128°. **2:2-Dibenzoyloxydibenzylidenacetone** separates from alcohol in glistening yellow leaflets, m. p. 124°. **2:2-Diethoxydibenzylidenacetone** forms glistening yellow leaflets, m. p. 89°. **2:2-Dibenzoyloxydibenzylidenacetone** forms yellowish-white crystals, m. p. 135°. A. Mck.

**Duplobenzylidenethioacetone and the Oxonium Theory.** HANS VON LIEBIG (*J. pr. Chem.*, 1907, [ii], 70, 277—280). A criticism of Fromm and Hoeller's views as the constitution of the addition compounds of duplobenzylidenethioacetone (this vol., i, 710) from the standpoint of the present author's view of the nature of oxonium salts (this vol., i, 45).

**Acetalation of Aldehydes and Ketones.** LUDWIG GRUBER (*Ber.*, 1907, 40, 3203—3214). In consequence of the experience of many investigators, the author publishes the details of his process for obtaining acetals in nearly quantitative yield from aldehydes or ketones by means of ethyl orthoformate. The aldehyde, or ketone (1 mol.) and ethyl orthoformate (1.1 mols.) are dissolved in alcohol (not more than 3 mols.) and the mixture, in the presence of a catalyst, such as a

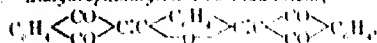
ordinary temperature or is gently warmed.

Esters of  $\beta$ -diketones and of the esters of ketonic acids are also obtained by this method. Benzoylacetone yields the ester,  $\text{C}_6\text{H}_5\text{CH}(\text{CO})\text{OEt}$ , b. p.  $162-164^\circ$ ,  $D_4^{20}$  1.058, which is converted by hydroxylamine into 3-phenyl 5-methylisoxazole, m. p.  $42-43^\circ$ .

If too large a quantity of the catalyst is used in the process, or if the time is unduly prolonged, the yield of the acetal may diminish to 50%.

Arnschott's experiments on the acetalization of acetone and acetophenone by ethyl orthoformate and alcohol without a catalyst (this vol. i, 749) have been repeated, and not a trace of the acetal has been obtained. C. S.

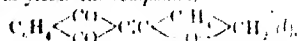
**Condensation of Diketohydrindene (1:3 Indandione) with Phthalic Anhydride.** CARMELLO MARCHESE (*Gazzetta*, 1907, 37, 393-399).—Anhydrophthalylbis 1:3 indandione,



prepared by the condensation of phthalic anhydride with 1:3 indandione or ethyl 2-sodio 1:3-diketohydrindene 2-carboxylate in presence of acetic anhydride, crystallises from xylene or nitrobenzene in yellow needles, m. p.  $325^\circ$ , and dissolves in alkali hydroxides, giving intensely red solutions.

Phthalylbis 1:3 indandione,  $\text{C}_{20}\text{H}_{12}(\text{CO})_2\text{CH}(\text{CO})_2\text{C}_6\text{H}_4$ , obtained by heating the preceding compound with alcoholic potassium hydroxide solution, separates from ethyl acetate in faintly yellow, shining crystals, m. p.  $198^\circ$ , and dissolves readily in nitrobenzene and sparingly in alcohol, benzene, xylene, or acetic acid. The salts of the alkali metals and of calcium are intensely red and readily soluble in water; the barium salt,  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Ba}, 11\text{H}_2\text{O}$ , was analysed.

Reduction of anhydrophthalylbis 1:3 indandione by means of zinc dust and acetic acid yields the compound,



m. p.  $275^\circ$ , which dissolves in acetic acid or ethyl acetate and, to a slight extent, in alcohol, water, benzene, or xylene.

An attempt to condense camphoric anhydride with 1:3 indandione in presence of acetic anhydride yielded 2-acetyl 1:3 indandione (compare Schwerin, Abstr., 1894, i, 194).

T. H. P.

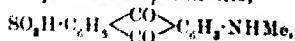
**New Anthraquinone Derivatives.** EDUARD LAURÉ (*Ber.*, 1907, 40, 3562-3567).—1-*p*-Bromoanthracanthraquinone, prepared by condensing anthracanthraquinone with *p*-dibromobenzene in presence of potassium carbonate and copper powder, is a dark red powder, m. p.  $305^\circ$ , dissolving in concentrated sulphuric acid with a green coloration which changes to a scarlet red on the addition of a drop of dichromate. *p*-Phenylenediaz 1-aminanthraquinone, obtained at the same time as the above compound, separates from chloroform as a blackish-violet powder giving a violet, metallic, glistening mark on porcelain, m. p. above  $320^\circ$ . 2-*p*-Bromoanthracanthraquinone forms ball-like, scarlet



1-Methylaminoanthraquinone reacts more easily with carbazole and with methylamine than the corresponding chloro-compound. 1-Methylaminoanthraquinone crystallises in well-formed, ruby-red crystals, m. p. 254°, dissolving in sulphuric acid with an emerald-green coloration which, on warming, changes through olive-green to brown. It then rises to a yellowish-red solution with green fluorescence, which is destroyed with zinc and acetic acid. 1-Diphenylaminoanthraquinone is a blackish-red powder, dissolving with an olive-green coloration in sulphuric acid.

[Preparation of Amino-, Alkylamino-, and Arylamino-derivatives of Anthraquinone.] FARBENFABRIKEN WERKE AG, BAYER & Co. (D.R.-P. 181722. Compare this vol., i, 111.)—The sulphonic groups in 1:5- and 1:8-anthraquinonedisulphonic acids may be partially or completely replaced by amino-, alkylamino-, or arylamino-groups by heating the alkali salts of these acids with ammonia, an alkylamine, or an aromatic amine.

*1:1-Methylaminoanthraquinone 5-sulphonic acid,*



is produced together with a small amount of *s*-dimethyl-1:5-dimethylaminoanthraquinone,  $\text{NHMe}\cdot\text{C}_6\text{H}_3\left\langle\begin{array}{c}\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}\end{array}\right\rangle\text{C}_6\text{H}_3\cdot\text{NHMe}$ , by heating potassium 1:5-anthraquinonedisulphonate with aqueous methylamine at 150°; the potassium salt crystallises from water in transparent needles.

*1:1-Methylaminoanthraquinone 8-sulphonic acid*, *1-aminoanthraquinone-8-sulphonic acid*, and *1-aminoanthraquinone-8-sulphonic acid* are similarly obtained, and their tinctorial properties are described in the patent.

*s*:1:5-*p*-Ditolylaminoanthraquinone may be prepared from 1:5-anthraquinonedisulphonic acid and *p*-toluidine. C. T. M.

**Preparation of Trichloroanthraflavio Acid.** R. WEDERHOF (D.R.-P. 181659).—The chlorine additive product of anthraflavio acid ("hexachloroanthraflavio acid"), when heated with glacial or any other solvent of high boiling point, such as xylene or nitrobenzene, loses hydrogen chloride and furnishes a *trichloroanthraflavio acid*, which separates in lustrous, yellow needles. This compound, which is employed in the preparation of dyes of the anthraene series, is insoluble in water, and yields a sparingly soluble sodium salt.

**Preparation of Dianthraquinonyl and its Derivatives.** ANILIN- & SODA-FABRIK (D.R.-P. 184495).—The following is an alternative method of preparing dianthraquinonyl and its derivatives. 1-Amino-2-methylanthraquinone is diazotised in sulphuric acid and the dry diazo-sulphate suspended in acetic anhydride

and heated  
phenyl is ob

**Preparation of a Chlorine Additive Compound of Anthraquinone Carboxylic Acid.** R. Wessman (D.R.-P. 179916).—Anthraquinone carboxylic acid does not absorb chlorine in acidified water at 100°, but when the boiling temperature is raised by the addition of sulphuric acid, chlorination occurs with the formation of the dichloro-derivatives; however, this acid is suspended in concentrated calcium or magnesium chloride solution and treated at 110° with a mixture of sodium chloride and hydrochloric acid, a yellow substance having the composition of a *hexachlorodihydroxyanthraquinone* is obtained. This compound is moderately stable towards acids, but is decomposed by alkalis and dilute alkalis. When heated in phenol or cresol, the additive product loses hydrogen chloride and a well-defined trichloroanthraquinone acid is produced. (G. T. M.)

**Benzanthrone Derivatives of the Naphthanthraquinone Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 181176). Oskar Auer, 1906, i, 889, and this vol., i, 324).—Naphthanthraquinone resembles anthraquinone in reacting with glycerol to yield benzanthrone derivatives, which on heating with alkali hydroxides furnish the colouring matters suitable for vat dyeing.

Benzonaphthanthrone,  $C_{21}H_{11}O$ , m. p. 186–188°, was prepared in the following ways: (1) by heating naphthanthraquinone with glycerol, alkali sulphate, and concentrated sulphuric acid at 150°, or by warming its dihydro-derivative with these reagents at 110°, (2) by heating the quinone or naphthanthranol with glycerol and zinc chloride at 150° to 210°. (G. T. M.)

**Linalool is a Tertiary Alcohol.** ROURE-BERTRAND. *Ann. Chem. Phys.*, 1907, ii, 464, from *Wied. u. ind. Ber. Roure-Berttrand*, Vol. (i, 5, 3–5).—Experiments on the formation of esters of geraniol and linalool have shown that linalool is a tertiary alcohol. The alcohols were mixed with acetic acid (6 mols.) and kept at a constant temperature. The quantities which had entered into combination after different periods are given below:

	hours			days			months	
	6.	24.	3.	19.	15.	21.	5.	12.
geraniol	27	55	12.6	29.2	35.7	45.9	85.6	90.0
linalool	—	0.6	—	0.6	—	1.1	3.9	5.3

E. W. W.

**Terpenes and Ethereal Oils. LXXXVI. Compounds of the Terpinene Series.** ORTO WALLACH and FRIEDRICH BORNACKER and, in part, FRITZ MEISTER [*Annalen*, 1907, 366, 197–226. Compare this vol., i, 64].—This paper contains a further account of the compounds of the terpinene series and their relationships to other terpenes. Part of the details have been already published (this vol., i, 217, 228, 229); the following are new.

is known to the monohydrochloride,  $C_{10}H_{17}Cl$ , and may also be formed from the dihydrochloride,  $C_{10}H_{17}Cl_2$ , and from the saturated alcohol,  $C_{10}H_{19}OH$ , from subinene hydrate, and from the monohydrochloride.

Terpinene monohydrochloride,  $C_{10}H_{17}Cl$ , b. p. 85—95°/12 mm., prepared by the action of hydrogen chloride on the terpinene in carbon disulphide solution, forms the dihydrochloride when treated with hydrogen chloride in glacial acetic acid. The monohydrochloride obtained from carbinene (this vol., i, 229) does not solidify in mixtures of solid carbon dioxide and ether, and is more stable towards potassium hydroxide than is limonene monohydrochloride.

The terpin,  $terpinolene$ ,  $C_{10}H_{16}$ , (this vol., i, 229) is prepared by shaking thujene or terpinol with sulphuric acid. Terpinol is formed as an intermediate product in the preparation of the terpin from carbinene. The terpin crystallises and sublimes in white leaflets, m. p. 127°/12 mm., b. p. 256° (slight decomposition), is markedly volatile with steam, is more readily soluble than *cis*-terpin hydrate, forms mixed crystals with about 10% with anhydrous *cis*-terpin, and with hydrogen chloride in glacial acetic acid forms terpinene dihydrochloride.

When distilled with a saturated solution of oxalic acid, terpinol yields terpinolene, which is obtained as a colourless oil, b. p. 172—173°,  $D_4^{20}$  0.897,  $n_D^{20}$  1.445, and is a mixture of solid carbon dioxide and ether, and is volatile with steam. Treatment with hydrogen bromide in light petroleum solution, or with terpinene dihydrobromide, gives a light red, crystalline precipitate with bromine in light petroleum, and on oxidation yields products different from those obtained from cineol.

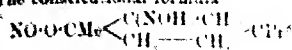
The terpinol obtained from caradimon and majorana oils must have the constitution  $CMc \begin{matrix} CH_2CH_2 \\ | \\ CH_2CH_2 \end{matrix} > CPr^2OH$ , since the trihydroxyterpane, m. p. 114—116°, obtained on oxidation with potassium permanganate, yields carvenone when heated with hydrochloric acid. The trihydroxyterpane,  $OH \cdot CMc \begin{matrix} CH_2CH_2 \\ | \\ CH_2CH_2 \end{matrix} > CPr^2OH$ , on oxidation with chromic acid, yields a small amount of a ketone which forms a semicarbazone,  $C_{10}H_{16}ON_2$ , m. p. 146°, and may be the ketone. No trihydroxyterpane is oxidised by potassium permanganate in alkaline solution, forming two isomeric acids. The acid,  $C_{10}H_{16}O_4$ , m. p. 205—206°, which is the main product, loses water when heated or when boiled with acids, forming a lactone,  $C_{10}H_{14}O_3$ , m. p. 63—64°.

This is volatile with steam, and on treatment with alkalis again forms the acid, m. p. 205—206°. The isomeric acid, m. p. 188—189°, yields a lactone,  $C_{10}H_{14}O_3$ , m. p. 72—73°, from which it is regenerated by the action of alkalis.

The terpinol from subinene has  $[\alpha]_D^{20} +25.4$ , and on oxidation yields a trihydroxyterpane,  $[\alpha]_D^{20} +21.21$ . Optically inactive terpinol, which on oxidation yields the acid, m. p. 188—189°, is obtained from terpinene dihydrochloride and from the fractions of commercial terpinol boiling at low temperatures. The terpinol from terpinene

terpene is reduced to a mixture of small amounts of  $\alpha$ -menthone-1-ol and  $\beta$ -menthone-1-ol.

The reduction of terpinene nitrosite in alkaline solution leads to the formation of a mixture of carvone and tetrahydrocarvone (compare Wallach and Laufer, Abstr., 1901, i, 89; Amenomiya, Abstr., 1903, i, 603). The constitutional formula



is assigned to the nitrosite, which, however, in view of its chemical behavior and in spite of the results of molecular weight determination, is considered to be bimolecular.

The paper concludes with a discussion of the constitution of terpinene.

G. Y.

**Sequiterpenes. I. Caryophyllene.** ERNST DRUSEN and ARTHUR LEWISOWITZ (*Annalen*, 1907, 350, 1-25). A study of caryophyllene was undertaken in continuation of the investigation of West Indian sandalwood oil (Abstr., 1900, ii, 379; 1902, i, 552).

Caryophyllene nitroschloride (m. p. 161-163°; Wallach and Walker, Abstr., 1893, i, 101; 158-160°; Schreiner and Kromers, Abstr., 1900, i, 106) is found to be a mixture, on extraction with alcohol containing 10% of ethyl acetate, a caryophyllene nitroschloride remains unchanged, and on recrystallisation from chloroform separates in glistening crystals, m. p. 177° if slowly or 179° if quickly heated; it is optically inactive, is stable, remaining unchanged when boiled with concentrated hydrochloric or nitric acids, and forms solutions in chloroform and benzene which are colourless at the ordinary temperature and become blue when heated. The alcohol-ethyl acetate extract contains  $\beta$ -caryophyllene nitroschloride, which crystallises in needles, m. p. 159°;  $[\alpha]_D^{20} = +28.07^\circ$ , is moderately soluble in hot light petroleum, and may be bimolecular, and a *substance*,  $\text{C}_{15}\text{H}_{24}\text{O}_2\text{N}$ , which crystallises in prismatic needles, m. p. 162.5-163.5°;  $[\alpha]_D^{20} = +217.2^\circ$ , is sparingly soluble in light petroleum, and decolorises bromine, but does not react with benzylamine. A caryophyllenenitroschloride reacts with benzylamine forming Schreiner and Kromers' *base*, m. p. 126-128° (*loc. cit.*), which therefore is a caryophyllenenitrosbenzylamine. The *hydrochloride*  $\text{NO} \cdot \text{C}_{15}\text{H}_{23} \cdot \text{NH} \cdot \text{CH}(\text{Ph}) \cdot \text{HCl}$ , crystallises in glistening leaflets, m. p. 125°, and is optically inactive.  $\beta$ -Caryophyllenenitrosbenzylamine, Schreiner and Kromers' *base*, m. p. 167°, is formed by the action of benzylamine on the  $\beta$ -nitroschloride; it crystallises from chloroform and alcohol in needles, m. p. 172-173°;  $[\alpha]_D^{20} = +217.87^\circ$ , and yields a laboratory *hydrochloride*.

$\alpha$ -Nitrocaryophyllene,  $\text{C}_{15}\text{H}_{22}\text{ON}$ , formed by reducing the  $\alpha$ -nitroschloride with sodium and methyl alcohol, crystallises in rhomboids, m. p. 115°, is optically inactive, and yields a crystalline *additive compound* with bromine.

$\beta$ -Nitrocaryophyllene, formed by reduction of the nitroschlorides, crystallises in needles, m. p. 120-121°;  $[\alpha]_D^{20} = +61.77^\circ$ .

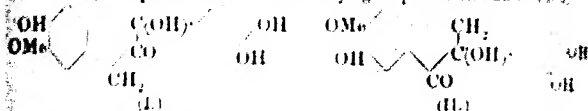
The blue caryophyllene nitrosite, m. p. 115°,  $[\alpha]_D^{20} = +102.95^\circ$ , when treated successively with potassium hydroxide and acetic acid in

obtained the resin formed by the action of alkalis on *eriodictyonone*, then a

When heated with fuming hydrochloric acid in a sealed tube at 120°, *eriodictyonone* yields catechol and an oil, which gives a green coloration with alcoholic ferric chloride, and is probably an isoprenol,  $C_{15}H_{26}O(OH)_2$ .

The action of diazomethane on *eriodictyonone* leads to the formation of a methyl ether,  $C_{15}H_{26}O_2(OMe)_2$ , which crystallises in prisms m. p. 160°, reduces ammoniacal silver solution, forms a red resin when heated with aqueous alkalis, and gives a red coloration with alcoholic ferric chloride. On further treatment with an excess of diazomethane, this ether yields the tetramethyl ether,  $C_{15}H_{26}O_2(OMe)_4$ , which crystallises in yellow needles, m. p. 162°, is insoluble in aqueous alkalis, and does not give a coloration with ferric chloride. When treated with potassium hydroxide, the tetramethyl ether forms protocatechuic acid.

In the light of these results, it is considered that the constitution of *eriodictyonone* must be represented by the formula I or II. In both cases, the position of the methoxyl group remains undetermined.



(see also Power and Tutin, *Proc.*, 23, 243).

G. Y.

**Spectrophotometry of the Chlorophyllins and the Energetics of Chlorophyll.** M. TSVET (Ber. deut. bot. Ges., 1907, A, 388-397. Compare this vol., i, 787). Results obtained with an alcoholic solution of chlorophyllin show that the absorption is greater in the blue portion of the spectrum than in the red. The band  $\lambda$  460-475 can be distinguished in solutions so diluted that the band in the red portion is no longer visible.

N. H. J. M.

**Phylloxanthin.** M. TSVET (*Biochem. Zeitsch.*, 1907, 6, 475-477).—A reply to Marchlewski's criticism (this vol., i, 867) of the conclusions drawn by the author (this vol., i, 787). The spectrum of phylloxanthin is very similar to that of  $\beta$ -chlorophyllin; neither substance can be transformed into phyllocyanin.

G. Y.

**New Method of Preparing Azophenin.** WLADIMIR S. RUBINOV (*Zeitsch. Farb. Ind.*, 1907, 6, 289-291).—Details are given for preparing quinonedichlorodimine by the action of a solution of bleaching powder on *p*-phenylenediamine or its hydrochloride; by the method used, a pure white product is readily obtained. It is best converted into azophenin by adding aniline to its solution in benzene; other substances are also formed, but azophenin is the principal product. 1.5 grams of azophenin from 3.5 grams of quinonedichlorodimine, and can be easily separated in a pure state.

W. A. P.

**Oxidation of Aromatic Amines by Means of Manganous Salt with Formation of Dyes.** FRITZ CRONER (*Chem. Zeit.*, 1907, 31, 948-949).—If 10 c.c. of a 0.2% aqueous solution of steryl

ammonium pentamethylarsenate] are treated with 10 drops of an aqueous manganese chloride solution free from iron and three drops of pyridine, and the resulting precipitate dissolved by addition of a moderate excess of sulphuric acid to the mixture, there is obtained a clear red solution. The red substance is not extracted by shaking with amyl alcohol. The coloration is not produced if the precipitate and reaction liquid are treated with acid separately. Colorations are obtained in the same manner with primary or secondary aromatic amines, but not with tertiary amines, nitroamines, or acylamines. These results confirm Ehrlich and Berthelm's formula for amyl (this vol., i, 812). Descriptions are given of the colorations produced with numerous aromatic amino and diamino compounds; where the resulting substance is soluble in amyl alcohol, the colour of the extract is also given.

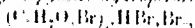
The amount of dye formed is proportional to the manganese salt and not to the alkali added. The colour reaction takes place in presence of arsenic chloride or arsenious acid, but is diminished in intensity by addition of small amounts of hydrogen cyanide or thiocyanate, and is suppressed completely when these are present in molecular proportion to the manganese salt. Similar colour reactions are obtained in this manner, but only in isolated cases with ferrous chloride; nickel, iron, and copper salts do not give colorations. G. Y.

**Methylfurfuralaldoxime.** Correction. WILHELM MEYER, *Ber.* 1907, 40 3567—3568. Compare this vol., i, 232.<sup>1</sup>—The compound,  $C_5H_7NO$ , previously regarded as a mixture of the *cis*- and *anti*-forms of the oxime, is now shown to be pure methylfurfuralaldoxime. E. F. A.

**Hydroperbromides of Negatively Substituted 4 Pyrones.** *Proc. East. Ber.* 1907, 40, 3647—3652. Compare Abstr., 1905, i, 134; 1906, i, 974. Contrary to Hantzsch and Denstorff's view that compounds having relatively strong basic properties are capable of forming hydroperbromides, crystalline, more or less stable hydroperbromides have been prepared from 4 pyrones with feeble or no basic properties.

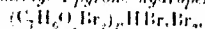
Hydroperbromides of bromo- and dibromo-2:6-dimethyl-4 pyrones were shown previously to exist in the crude product of the action of ethylated bromine on 2:6-dimethyl-4 pyrone; the composition of this crude product is found now to have undergone little change in two years. The pure hydroperbromides are prepared by the action of bromo- and hydrogen bromide on bromo- and dibromo-2:6-dimethyl-4 pyrones.

1. *Bromo-2:6-dimethyl-4 pyrone hydroperbromide*,



is a yellow, crystalline powder, decomp. 159°.

2. *Dibromo-2:6-dimethyl-4 pyrone hydroperbromide*,



decomp. 147—148° when freshly prepared, decomposes only slowly at

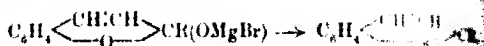
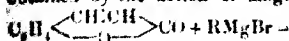
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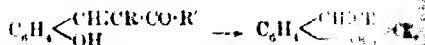
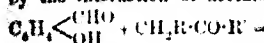
form crystalline masses, which are easily separated from the mother liquor.

Ethyl chelidonate and ethyl dibromochelidonate form hydroperbromides,  $C_{11}H_{13}O_6HBr.Br$ , and  $C_{11}H_{13}O_6HBr_2.HBr.Br$ , respectively, which crystallize in reddish-brown needles or prisms, but are less stable than the hydroperbromides of the brominated dimethyl compounds, decomposing when washed with ether or light petroleum or on exposure to air, evolving fumes of bromine and hydrogen bromide.

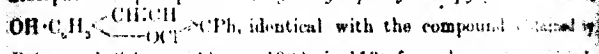
**Synthesis of Benzopyrylium Derivatives.** HENRI BULO and THEODOR VON FELLENBURG (*Ber.*, 1907, 40, 3815—3817). Benzopyrylium derivatives may be prepared by the method employed by Binsly and Decker (Abstr., 1904, i, 912) in the synthesis of pyrylium compounds; thus, 2-substituted benzopyrylium compounds may be obtained by the action of magnesium alkyl bromides on benzaldehyde.



They also result from the ring condensation of the products obtained by the interaction of acetaldehyde or ketones and salicylaldehyde:



Hydrogen chloride passed into a mixture of resorcinol and acetophenone precipitates 7-hydroxy-2-phenylbenzopyrylium picrate.



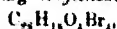
Bulow and Sicherer (Abstr., 1902, i, 113) from benzoylacetate and resorcinol. The compounds obtained by Bulow (Abstr., 1902, i, 400, 559; 1902, i, 113) from 1:3-diketones and dihydroxyacetone are therefore hydroxybenzopyrylium salts. The formula of these compounds must consequently contain 1 mol. of water, i.e., that is present in the formula assigned to them by Bulow; this mol. of water is really present as water of crystallization.

7-Hydroxy-2-phenylbenzopyrylium picrate loses its water of crystallization at 100° without undergoing decomposition as stated by Bulow and Sicherer (*loc. cit.*). W. H. P.

**Synthesis of Leuco-coumaranones.** STANISLAV KOVATANECKI, VICTOR LAMPE, and CH. MARSCHALK (*Ber.*, 1907, 40, 3660—3669).—The synthesis of *p*-benzoylcoumarans was attempted in order to throw further light on the constitution of catechin (compare the vol. i, 73). Two methods were tried: (1) the conversion of hydroxybenzophenone into the corresponding coumaran derivative, (2) the action of aromatic acid chlorides in the presence of aluminum chloride

as common. It is not yielded by the action of hydrazine, benzophenone, and ethylene dichloride in sodium methoxide, 3-chloro-4- $\beta$ -bromomethylbenzophenone,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{COPh}$ ,

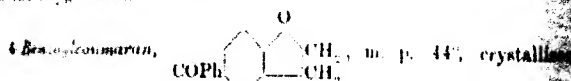
is formed as chief product. It crystallises in small, white plates, m. p. 177°. There is also formed the sparingly soluble 4:4'-di- $\beta$ -bromo-3-chlorobenzophenone,  $\text{C}_{12}\text{H}_8(\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COPh})_2$ , crystallising in white needles, m. p. 224—226°. All attempts, however, to close the benzene ring by the Wurtz reaction were unsuccessful, and the same remark applies to the bromo-derivatives. 3-Bromo-4- $\beta$ -bromomethylbenzophenone,  $\text{C}_{12}\text{H}_8\text{O}_2\text{Br}_2$ , crystallises in white leaflets from dilute alcohol, m. p. 96—97°; the 4:4'-ethylenedioxy-bis 3-bromobenzophenone,  $\text{C}_{12}\text{H}_8\text{O}_4\text{Br}_2$ , m. p. 229—230°. 3,5-Dibromo-4- $\beta$ -bromomethylbenzophenone,  $\text{C}_{12}\text{H}_8\text{O}_2\text{Br}_3$ , crystallises in white plates, m. p. 105—107°, the corresponding ethylenedioxy derivative,



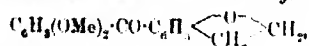
has m. p. 217—218°.

4- $\beta$ -Bromomethylbenzophenone,  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{Br}$ , which crystallises in prisms from alcohol, m. p. 72°, does not yield *p*-benzoylcoumaran on treatment with aluminium chloride; the product obtained is *p*-benzylphenol. The corresponding ethylenedioxy compound,  $\text{C}_{12}\text{H}_{12}\text{O}_4$ , has m. p. 100°.

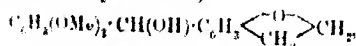
Coumaran itself reacts easily with aromatic acid chlorides in the presence of aluminium chloride and from analogy to the phenol ethers, the conclusion is drawn that substitution occurs in the para-position to the oxygen atom.



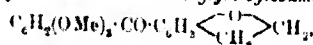
from light petroleum in the triclinic system [ $a:b:c = 1.4568:1:1.8354$ ;  $\alpha 101.52^\circ$ ,  $\beta 109.45^\circ$ ,  $\gamma 103.9^\circ$ ]. By reduction of an alcoholic solution, the leuco-*p*-benzoylcoumaran was obtained as a viscous oil; it is conjectured to be the parent substance of catechin. 4-Veratroylcoumaran,



crystallises in stout, white prisms, m. p. 136—137°, and gives on reduction leuco-4-veratroylcoumaran,



in stout prisms, m. p. 97—98°. 2-Trimethylgalloylcoumaran,



forms needles, m. p. 110—111°, and its leuco-compound,  $\text{C}_{14}\text{H}_{20}\text{O}_7$ , forms leaflets, m. p. 108—109°.

Coumaran also combines with acid chlorides to form similar derivatives. 6-Benzoylchroman,  $\text{C}_{16}\text{H}_{14}\text{O}_2$ , is an oil, b. p. 365°/710 mm., solidifying to a crystalline mass in a cold mixture. 6-Veratroyl-



chromone,  $C_8H_6(OMe)_2 \cdot CO \cdot C_6H_5$ ,  $\begin{matrix} & & CH_2 & CH \\ & & / & \backslash \\ & & C & C \end{matrix}$ , crystallises in white needles, m. p. 103–104°; its *leuco* compound,  $C_{18}H_{20}O_4$ , forms prisms, m. p. 115–116°.

The following compounds are also described: *p*-*tert*-butyl anisole,  $C_6H_5(OMe)_2 \cdot CO \cdot C_4H_9$ , EtOMe, which crystallises in white needles, m. p. 103–104°, and its *leuco* derivative,  $C_{18}H_{20}O_4$ , which crystallises in white needles, m. p. 84–85°; *p*-trimethylgalloyl-*o*-ethylaniide,  $C_{17}H_{20}O_6$ , m. p. 107–108°, the *leuco* compound has m. p. 86–88°.

#### Further Synthesis in the Flavone Group. STANLEY

KORTANECKI (*Ber.*, 1907, 40, 3669–3677). (With M. F. KORTANECKI.) 6-Hydroxy 4-isopropylflavone,  $C_{17}H_{14}O_3$ , prepared by the introduction of quinaacetophenone monomethyl ether, cumenol, and sodium in alcohol, crystallises from alcohol in colourless leaflets, m. p. 90°.

6-methoxy 4-isopropylflavone,  $OMe \cdot C_6H_3 \begin{matrix} & & O & CH \cdot C_6H_4 \cdot Pr \\ & & / & \backslash \\ & & C & CHBr \end{matrix}$ , obtained

by brominating the corresponding methoxyisopropylflavone with carbon disulphide, forms white needles, m. p. 125–127°. It and 3-bromodavanones when treated with concentrated potassium hydroxide in alcoholic solution, hydrogen bromide is eliminated.

6-methoxy 4-isopropylflavone,  $OMe \cdot C_6H_3 \begin{matrix} & & O & CH \cdot C_6H_4 \cdot Pr \\ & & / & \backslash \\ & & C & CH \end{matrix}$ , is obtained

it crystallises from dilute alcohol in white leaflets, m. p. 147°. On heating with hydrochloric acid, 6-hydroxy 4-isopropylflavone,  $C_{17}H_{14}O_3$ , is formed, and from alcohol gives pale yellow needles, m. p. 182–183°.

[With A. TÖBLER.] 2-Hydroxy 4-methoxy 4-isopropylflavone,  $OMe \cdot C_6H_3(OH) \cdot CO \cdot CH(CH_3) \cdot C_6H_4 \cdot Pr$ , prepared by condensing cumenol with paeonol, crystallises in alcohol in yellow leaflets, m. p. 104°.

When an alcoholic solution of this compound is heated with dilute hydrochloric acid for twenty-four hours, it is transformed into 7-methoxy 4-isopropylflavone,  $OMe \cdot C_6H_3 \begin{matrix} & & O & CH \cdot C_6H_4 \cdot Pr \\ & & / & \backslash \\ & & C & CH \end{matrix}$ , which crystallises in prisms, m. p. 75°. Amyl nitrite and hydrochloric acid convert the flavanone into the isonitroso derivative, which, however, is unstable, and there results 7-methoxy 4-isopropylflavone,  $OMe \cdot C_6H_3 \begin{matrix} & & O & CH \cdot C_6H_4 \cdot Pr \\ & & / & \backslash \\ & & C & CH \end{matrix}$ ; it crystallises in yellow glistening leaflets, m. p. 201°.

Like all flavanols, the yellow salt is sparingly soluble; the acetate,  $C_{22}H_{26}O_6$ , has m. p. 163°. Reduction of the methoxyisopropylflavanol with hydriodic acid gives 7-hydroxy 4-isopropylflavanol,  $C_{17}H_{16}O_3$ , which forms colourless leaflets, m. p. 213°; the diacetate,  $C_{22}H_{26}O_6$ , crystallises in white needles, m. p. 124°.

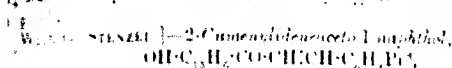
With H. RAJASOWITSEN. 2-Hydroxy 3:4-dimethoxy 4-isopropylflavone,  $OMe \cdot C_6H_3(OMe) \cdot CO \cdot CH(CH_3) \cdot C_6H_4 \cdot Pr$ , prepared from quinaacetophenone, dimethyl ether and cumenol in the presence of

by sodium hydride, crystallises in yellow leaflets, m. p. 110°, and forms the starting point for the preparation of the 7:7-dihydroisopropylflavanol in a similar manner to that of the dihydro compound.

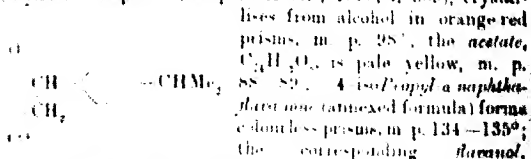
7:7-dihydro-4-isopropylflavanose,  $C_{15}H_{20}O_2$ , forms small, white, prismatic crystals, m. p. 92°. The isonitroso derivative,  $C_{15}H_{21}O_2N$ , is also a leaflet, m. p. 175°.

7:7-dihydro-4-isopropylflavanol,  $C_{15}H_{20}O$ , forms pale yellow needles, m. p. 102°, and yields an intensely yellow sodium salt; the acetate,  $C_{17}H_{22}O_3$ , white needles, m. p. 152°.

7:7-dihydro-4-isopropylflavanol,  $C_{15}H_{20}O$ , crystallises in glistening leaflets, m. p. 265°; the diacetate,  $C_{17}H_{22}O_4$ , forms white needles, m. p. 152°.



prepared from cinnenol and 2-acetophenanthridin under similar conditions to the pale compound (compare Abstr., 1898, i, 369), crystallises from alcohol in orange-red



**Preparation of Santalyl Esters.** CHEMISCHE FABRIK VON BERG (AKTION GESELLSCHAFT) (D.R. P. 182627). Compare Abstr., 1904, 272. The santalyl esters of the higher fatty acids from lauric acid onwards do not possess the unpleasant odour and irritating properties of free santalol and its esters with acetic acid and immediate homologues.

Santalyl acetate, a clear yellow oil, is prepared by mixing santalol with acetyl chloride and completing the reaction on the water-bath; separates on the addition of alcohol.

Santalyl valerate and santalyl oleate resemble the preceding compound and are prepared respectively in a similar manner from valeryl chloride and santalol.

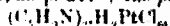
G. T. M.

**Preparation of Thionaphthen Derivatives.** KALLE & Co. (B.P. 184020).—*o*-Aminophenylthioglycollic acid, prepared from benzidine and chloroacetic acid, when diazotised and treated with benzene cyanoperoxide furnishes *o*-cyanophenylthioglycollic acid, white needles, m. p. 142°. This substance on hydrolysis with benzene calcium hydroxide yields 3-amino(1)thionaphthen-2-carboxylic acid, which on further treatment with alkali gives rise to 3-hydroxy-

Some New Alkaloids from Plants. **ANT. PICTET** and **CH. OBER** (*Ber.*, 1907, 40, 3771—3783; *Bull. Soc. chim.*, 1907, [5] 1, 1001—1016).—The hypothesis put forward by Pictet (*Ann.*, 1906, 4, 841) receives support from the fact that alkaloids of simple structure are obtained by steam distillation from plants which have been treated with dilute sodium carbonate solution.

The concentrated aqueous extract of tobacco leaves ("raw tobacco") yields, when distilled at 80—120°, an alkaline distillate from which pyrrolidine and 1-methylpyrrolidine were isolated and identified by means of their auric and platinum chlorides. 1-Methylpyrrolidine *picrolonate* crystallises in yellow prisms, m. p. 322° (decomp.).

Black pepper yields a distillate which does not contain pyrrolidine as stated by Johnston (Abstr., 1889, 298), but a *base* which is probably a C-methylpyrrolidine,  $C_5H_9N$ ; the *aurichloride*,  $C_5H_9N.HAuCl_4$ , crystallises in yellow leaflets or flat needles, m. p. 183°; the *picrolonate* is a yellow, crystalline powder, m. p. 217°; the *platinichloride*,



m. p. 203°, forms microscopic, orange prisms.

The distillate from carrot leaves was found to contain pyrrolidine and a new base, *daucine*,  $C_5H_9N$ , a colourless, oily liquid with a nicotine-like odour, b. p. 240—250°,  $[a]_D^{20} + 7.74$  in ether. The *hydrochloride* forms long needles; no precipitate is produced on adding auric, platinum, or mercuric chloride to a solution of the hydrochloride. The hydrochloride when heated with zinc dust does not give a coloration with a pine shaving. The *base* obtained from carrot seeds is not identical with daucine, since it gives the pyrrole reaction and its *aurichloride*, m. p. 172—175° (decomp.), is insoluble.

The leaves of parsley yield a *base*, the crystalline *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust; no precipitate is obtained on adding auric or platinum chloride to a solution of the hydrochloride; the *picrolonate* forms yellow, microscopic needles, m. p. 210°.

Cocoa leaves yield a *base*, the *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust. No precipitate is formed on adding auric acid, auric or platinum chloride to a solution of the hydrochloride. Picrolonic acid produces a yellow, flocculent precipitate.

The authors consider that, since the above bases, with the exception of daucine, belong to the pyrrole group, they are probably derived from the plant albumin.

W. H. G.

Cinchona Alkaloids. VII. A New Oxidation Product of Cinchonine. **PAUL RARE** [with **ERNST ACKERMANN** and **W. SCHRAMM**] (*Ber.*, 1907, 40, 3655—3658).—An intermediate product of the oxidation of cinchonine by chromic acid in either sulphuric acid or glacial acetic acid has been isolated in small quantity. It is a base

$C_{10}H_{15}ON_3$ , and crystalline. The hydrochloride,  $C_{10}H_{15}ON_3HCl$ , is a white, crystalline solid, m. p. 245–247°; the methiodide,  $C_{10}H_{15}ON_3CH_3I$ , is a white, crystalline solid, m. p. 232–233°; the hydrobromide is oily. The base combines with hydroxylamine. W. R.

**True and False (Pseudo-) Commercial Tannates of Quinine.** FARRÉ, BONNELLI (*Gazzetta*, 1907, 37, ii, 205–226).—Tannic acid is capable of forming, with the ordinary salts of quinine, additive compounds which are usually yellow, containing proportions of tannic acid, are always obtained when solutions of tannic acid act on quinine salts. Many of the commercial quinine tannates are compounds of this nature, retaining some of the qualities of the quinine salts from which they have been prepared, and are hence termed pseudo- or false tannates. Quinine pseudo-tannates of constant composition can be prepared under constant conditions. The percentage of quinine in these compounds varies from 18 to 33. Tannic acid is not capable of displacing sulphuric or hydrochloric acid from the combination with quinine. True quinine tannates can only be prepared by mixing solutions of the base and acid in proportions varying according to the tannate required.

The following compounds have been prepared and analysed:  
 1) True quinine tannates:  $C_{20}H_{27}O_9N_2 \cdot C_{12}H_{10}O_5 \cdot 3H_2O$ ;  
 $C_{20}H_{27}O_9N_2 \cdot 2C_{12}H_{10}O_5 \cdot 6H_2O$ ;  $C_{20}H_{27}O_9N_2 \cdot 3C_{12}H_{10}O_5 \cdot 10H_2O$ .  
 2) False or pseudo tannates:  $4(C_{20}H_{27}O_9N_2 \cdot H_2SO_4 \cdot 5C_{12}H_{10}O_5 \cdot 15H_2O)$ ;  
 $2(C_{20}H_{27}O_9N_2 \cdot H_2SO_4 \cdot 5C_{12}H_{10}O_5 \cdot 26H_2O)$ ;  
 $2(C_{20}H_{27}O_9N_2 \cdot H_2SO_4 \cdot 5C_{12}H_{10}O_5 \cdot 25H_2O)$ ;  
 $2(C_{20}H_{27}O_9N_2 \cdot H_2SO_4 \cdot 5C_{12}H_{10}O_5 \cdot 20H_2O)$ ;  
 $2(C_{20}H_{27}O_9N_2 \cdot 2HCl \cdot 5C_{12}H_{10}O_5 \cdot 13H_2O)$ ;  
 $C_{20}H_{27}O_9N_2 \cdot 2HCl \cdot 5C_{12}H_{10}O_5 \cdot 4H_2O$ . T. H. P.

**A Base Obtained in the Working Up of the Alkaloids Occurring with Cocaine.** CARL LIEBERMANN (*Ber.*, 1907, 40, 2407–2408). Anhydroecgonine ethyl ester (Einhorn, Abstr., 1887, 74), Willstätter, Abstr., 1901, i, 649) has been found in the ecgonine residues obtained in the separation of the sub-idiary alkaloids of crude cocaine. It is formed probably by esterification of anhydroecgonine during the process of separation. The ethyl ester, b. p. 127–128°/11 mm.,  $[\alpha]_D^{20} -51.33$ , is hydrolysed by boiling hydrochloric acid, D 1.125, forming anhydroecgonine. The *picrate*,  $C_{20}H_{27}O_9N_2 \cdot C_6H_3O_7N_3$ , crystallises in yellow leaflets, m. p. 168°; the *picnate* salt, m. p. 217° (211°: Einhorn, *loc. cit.*); the *aurichloride*,  $C_{20}H_{27}O_9N_2 \cdot HAuCl_4$ , forms lemon-yellow granules, m. p. 124°.

**Codeine.** ALBERT LANGE (Ber., 1907, 40, 3781—3784; Chem. Abstr., 1906, 1, 692).—In consequence of Isidor's discovery that the high rotatory power of synthetic codeine is due to the presence of allylpiperidine, the author has attempted to prepare the alkaloid by a method which excludes the formation of the allyl compound. Methylpicrylalkaline is reduced by hydriodic acid and a solution of phosphorus at 125°, the product treated with zinc dust and acid water, and the resulting propylpyridine reduced by sodium and acid water to propylpiperidine, which is resolved by tartaric acid. The resulting base is pure isocodeine, and has  $[\alpha]_D^{25} + 17.85$ .

**Morphine.** XIV. **allo-Codeine, a New Isomeride of Codeine.** LUDWIG KNORR, HEINRICH HORLEIN, and CLARA SCHRYVER (Ber., 1907, 40, 3844—3851).—It has been lately pointed out by Knorr and Horlein (this vol., i, 789) that, of the two isomerides,  $\psi$ -codeine and isocodeine, quoted in the literature as being identical with codeine,  $\psi$ -codeine is a structural isomeride of codeine. The uncertainty exists, however, regarding Schryver and Lees' isocodeine (Trans., 1901, 79, 576), which is a mixture containing variable amounts of  $\psi$ -codeine, the presence of the latter doubtless accounting for the  $\psi$ -codeinone obtained by the oxidation of "isocodeine." In attempting to prepare pure isocodeine, the authors have obtained a new base, isomeric with codeine; crude isocodeine appears to contain isocodeine,  $\psi$ -codeine, and small amounts of this new base, which, for the present, is termed *allo-Codeine*. When this new base is treated with chromic acid in sulphuric acid solution, it forms  $\psi$ -codeinone, and accordingly contains the alcoholic hydroxyl group in position 4.

The melting points and specific rotations of the isomeric morphine, codeine, and methylmorphinemethines are quoted in tabular form, and also the melting points and specific rotations of the corresponding methiodides.

From the products of the hydrolysis of chloromorphide,  $\gamma$ -morphine, a new isomeride of morphine, has been isolated. The compound has m. p. 278°,  $[\alpha]_D^{25} - 91^\circ$  (solvent not stated), and its methiodide has m. p. 295° and  $[\alpha]_D^{25} - 51^\circ$ ; when methylated it becomes  $\psi$ -codeine [compare, however, Lees (Trans., 1907, 91, 1408), who has also lately studied the hydrolysis of chloromorphide and obtained as one of the products, neo-isomorphine, which seems to be identical with the above-mentioned  $\gamma$ -isomorphine].

*allo-Codeine* is possibly identical with Lees'  $\beta$ -isocodeine. It is prepared as follows from the mixture of bases obtained by the method of Schryver and Lees by the hydrolysis of bromocodide. Potassium iodide is added to the solution of this crude isocodeine in dilute acetic acid, when a mixture of  $\psi$ -codeine and *allo-Codeine* hydrochlorides gradually separates and may be separated by means of absolute alcohol. As an alternative method, crude isocodeine is acetylated by means of boiling acetic anhydride and the mixture of *allo-Codeine* acetates separated by means of absolute alcohol, in which *allo-Codeine* acetate is soluble with difficulty, and separates in this manner. m. p. 194—195°.

*allo*- $\gamma$ -codeine, obtained either from the hydriodide or the acetyl derivative, is an oil with a bluish-violet fluorescence; it has not yet been obtained crystalline. In absolute alcohol, it has  $[\alpha]_D^{25} = -358$  ( $c = 4.5$ ). Its hydriodide separates from water in spear-shaped crystals melting at  $260-265^\circ$ ; in aqueous solution, it has  $[\alpha]_D^{25} = -183$  ( $c = 1.77$ ). It differs from  $\gamma$ -codeine hydriodide, which crystallises from water in glistening leaflets, contains  $11\frac{1}{2}\text{H}_2\text{O}$ , has m. p.  $260-265^\circ$ , and  $[\alpha]_D^{25} = -57^\circ$ .

When *allo*- $\gamma$ -codeine is oxidised, it forms  $\gamma$ -codeinone.

*Acetalle*- $\gamma$ -codeine crystallises from absolute alcohol in needles, m. p.  $141-125^\circ$ , and differs from acetyl- $\gamma$ -codeine, which is an oil, and from acetylcodeine, which has m. p.  $133.5^\circ$ . Its methiodide,  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{MeI}, \text{EtOH}$ , separates from absolute alcohol in leaflets, m. p. about  $260^\circ$  (decomp.).

*Acetalle*-codeine methiodide,  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{MeI}$ , crystallises from methyl alcohol in rectangular leaflets, m. p. about  $215^\circ$  (decomp.). In aqueous solution, it has  $[\alpha]_D^{25} = -142^\circ$  ( $c = 1.728$ ). When boiled with sodium hydroxide, it forms a methine base which, for the present, is termed  $\gamma$ -methylnormorphinethine; it is apparently related to  $\epsilon$ -methyl-normorphinethine in the same manner as *allo*- $\gamma$ -codeine is related to  $\gamma$ -codeine. The new base has  $[\alpha]_D^{25} = -174$  ( $c = 8.91$ ) in alcoholic solution after treatment with alcoholic potassium hydroxide; when dried until constant in weight, it gave  $[\alpha]_D^{25} = -178$  ( $c = 10.955$ ) in aqueous solution. Its methiodide,  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{MeI}$ , is a colourless powder, m. p. about  $180^\circ$  (indefinite); in aqueous solution, it has  $[\alpha]_D^{25} = -148$  ( $c = 2.486$ ). A. McK.

**Morphine. XV. Dioxycodeine and Deoxydihydrocodeine.**  
 (From Knorr and Rudolf Wærentz (*Ber.*, 1907, 40, 3860-3868).

In continuation of the work of Knorr and Hürlein (this vol., i, 235), we found that deoxycodeine is best prepared by the reduction of oxycodide or chlorocodide with zinc dust and alcohol in the absence of acid. The reduction product, obtained by means of sodium and alcohol, is, however, not identical, as was formerly supposed, with the product obtained by the action of zinc and hydrochloric acid or of zinc dust and alcohol; it is levorotatory, whereas the other products are dextrorotatory.

From the dextrorotatory deoxycodeine of Knorr and Hürlein, the levorotatory base, deoxydihydrocodeine, is obtained by the action of sodium and alcohol.

Deoxycodeine melts at about  $126^\circ$  and crystallises from dilute methyl alcohol in glistening, hexagonal or rhombic leaflets. In alcoholic solution, it has  $[\alpha]_D^{25} = +119-121^\circ$  ( $c = 4.9215$ ).

*Deoxycodeine hydrochloride*,  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}, \text{HCl}, \text{EtOH}$ , crystallises from absolute alcohol in glistening prisms, which soften at about  $165^\circ$ , and have m. p. about  $270^\circ$  (decomp.); in aqueous solution, it has  $[\alpha]_D^{25} = +84-87^\circ$ . The hydriodide,  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}, \text{HI}$ , separates from water in needles, m. p. about  $265^\circ$  (decomp.). The benzoate crystallises from water in tiny, prismatic needles, m. p. about  $188^\circ$ ; in absolute alcohol, it has  $[\alpha]_D^{25} = +106^\circ$  ( $c = 5.53$ ). The acetyl derivative is an oil, and forms

$C_{15}H_{21}O_2N$ , Mel. 210°.  
crystallises from absolute alcohol in yellow needles, m. p. 210°.

Deoxycodine forms a glassy methiodide, from the aqueous solution of which a brown oil separates on boiling with sodium hydroxide. When this oil is crystallised from absolute alcohol, it forms needles, m. p. 162–164°, and is the methine base of deoxycodine. It is readily oxidised even at the ordinary temperature by the action of nitric acid,  $C_{15}H_{21}O_2N.HNO_3$ , is, however, more stable and separates from acetic acid in silky needles, m. p. 202°.

*Methyldeoxycodine methiodide*,  $C_{15}H_{23}O_2N.MeI$ , obtained by the methylation of deoxycodine in alkaline solution with methyl sulphate and interaction of the product with potassium iodide, crystallises in glistening leaflets, m. p. 251–252°, with potassium softening. It has  $[\alpha]_D^{25} + 108^\circ$  ( $c = 2.230$ ) in alcoholic solution.

When the aqueous solution of methyldeoxycodine methiodide is boiled with sodium hydroxide, an oil separates, which is very unstable; it decomposes in hydrochloric acid solution, giving dimethylmorphol.

*Deoxydihydrocodeine*,  $C_{17}H_{23}O_2N.H_2O$ , crystallises from dilute methyl alcohol in glistening leaflets, m. p. about 132°; the anhydrous compound has  $[\alpha]_D^{25} - 24^\circ$  ( $c = 5.171$ ) in absolute alcoholic solution. Its *hydrochloride*,  $C_{17}H_{23}O_2N.HCl.EtOH$ , has m. p. about 154° (decomp.), and  $[\alpha]_D^{25} - 17^\circ$  ( $c = 5.289$ ) in aqueous solution. The base separates from ethyl acetate in tetrahedra, m. p. about 186°, and has  $[\alpha]_D^{25} - 9^\circ$  ( $c = 5.145$ ).

*Methyldeoxydihydrocodeine methiodide*,  $C_{17}H_{25}O_2N.MeI$ , obtained by methylating deoxydihydrocodeine with methyl sulphate and then causing the product to react with potassium iodide, separates from water in leaflets and from alcohol in needles, m. p. 245–246° (indefinite), and has  $[\alpha]_D^{25} - 12^\circ$  ( $c = 2.773$ ) in 90% alcoholic solution.

A. M. K.

**Preparation of Narceine and Homonarceine Derivatives.** KROLL & Co. (D.R.-P. 183589). Compare this vol., i, 236. Narceine and homonarceine were formerly alkylated by treatment with alkyl sulphates, and it is now found that the same derivatives are obtained by the action of alkyl iodides, methyl phosphate, and methyl nitrate.

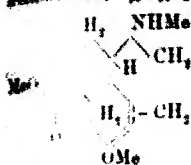
Ethylnarceine hydrochloride, m. p. 231°, may be obtained from the product of the interaction of ethyl bromide on the potassium derivative of narceine.

Methylnarceine hydrochloride, m. p. 243°, is produced by treating the potassium derivative of narceine with methyl phosphate, and combining the resulting base with hydrochloric acid.

G. T. M.

**The Action of Ozone on Thebaine.** ROBERT P. BARKER and HARRIS KIRKMAN (*Ber.*, 1907, 40, 3652–3654).—Morphine bases are converted into phenanthrene derivatives by treatment with ozone.

the side chain, however, being  $\text{C}_6\text{H}_5\text{NMe}_2$ . The molecular field of the alkaloid,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ , leaflets, m. p. 117° (corr.), contains two atoms of oxygen more than theobaine. The compound contains two methoxyl groups like theobaine, but the presence of a carbonyl group is shown by the formation of a monoximate,  $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}_2$ , which crystallises in flat rods, m. p. 120° (corr.). On dissolution of the theobaine in dilute sodium hydroxide solution, hydrolysis of one methoxyl group occurs, and the conclusion is drawn that one of the methoxyl groups exists as the ester. The fifth oxygen atom is indifferent. These results, taken in conjunction with those already known about theobaine, lead to the constitution annexed, the grouping  $\text{C}(\text{OMe})\text{C}$  being converted into that represented by  $\text{C}(\text{OMe})\text{CO}$ .



W. H.

**A New Base from the Solanaceae.** RICHARD WILLSTATTE and WILHELM HEUSSEN (*Ber.*, 1907, 40, 3869—3875). — The new alkaloid,  $\text{C}_8\text{H}_{12}\text{N}_2$ , obtained from *Hyoscyamus muticus* in addition to hyoscyamine and other products, is a colourless liquid, b. p. 111° (corr.), and with  $D^{20}_D$  0.7941; it is miscible with water in all proportions, has a strongly alkaline reaction, and is easily volatile with steam. It exhibits the behaviour of a saturated, ditertiary base. It is quite stable towards permanganate in cold sulphuric acid solution, and does not react with benzenesulphonic chloride and alkali. In moderate doses, it has no poisonous action. The hydrochloride,  $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{HCl}$ , crystallises in triangular prisms, m. p. 273° (decomp.), is deliquescent, and very readily soluble in water. Its platinumchloride,



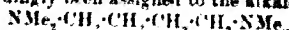
has m. p. 231° (decomp.); its aurichloride decomposes at 206—207°.

The compound,  $\text{C}_8\text{H}_{12}(\text{NMe}_2)_2$ , forms hygroscopic leaflets or tiny needles, m. p. 305—308° (decomp.). By the distillation of the ammonium base, obtained from the iodide by means of silver oxide, an aqueous distillate was obtained and a gas, which was identified as butadiene by means of the sparingly soluble a bromide, m. p. 117°, and the more easily soluble bromide, m. p. 39°. The aqueous distillate contained, in addition to trimethylamine, tetramethyldiaminobutane, which was identified by means of its aurichloride.

The preparation of 1:4-diaminobutane from succinaldioxime is described, the method used being a modification of the method of Cassaigne and Zanetti. The methylation of 1:4-diaminobutane is described, hexamethyltetramethylenediammonium chloride being obtained. When the latter compound is distilled, the main product is the monoamine, 1-methylpyrrolidine. 1-Methylpyrrolidine methiodide,  $\text{C}_5\text{H}_{11}\text{NI}$ , crystallises in prisms, which decompose above 300°; the aurichloride,  $\text{C}_5\text{H}_{11}\text{NCl}_2\text{Au}$ , crystallises in hexagonal prisms with pyramidal ends, m. p. 286° (decomp.).



The product of the methylation of *solanum* alkaloid is in the form of its chloride, aurichloride, platinichloride, and picrate, and compared with the quaternary derivatives of the solanum alkaloid has been investigated, the agreement being complete. The following constitution has accordingly been assigned to the alkaloid:



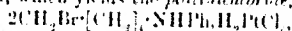
*Hexamethyltetramethylenediammonium chloride*,  $\text{C}_6\text{H}_{15}\text{N}_2\text{Cl}$ , crystallises from alcohol in prisms; its *picrate* has m. p. 285°; its *platinichloride* has m. p. 279° (decomp.); its *aurichloride* has m. p. 304–309°.

A. M. S.

**Rupture of Cyclic Bases by Cyanogen Bromide** (J. B. BAIRD, *Ber.*, 1907, 40, 3914–3933). The action of cyanogen bromide on cyclic bases either breaks the ring (Abstr. 1909, i, 439) or replaces the alkyl or aryl group attached to the nitrogen atom by the cyanogen group (Abstr. 1902, i, 365). A third alternative is represented by the scheme  $\text{X} \langle \bigcirc \rangle \text{N} \cdot \text{R} + \text{Br} \cdot \text{CN} = \text{Br} \cdot \text{X} \cdot \text{NR} \cdot \text{CN}$ . The reported

methods for the preparation of *ω*-dibromobutane and *ω*-bromopentane (Abstr., 1904, i, 841) have enabled the author to prepare numerous derivatives of pyrrolidine and piperidine, by means of which he has shown that the rupture of a cyclic base is more easily accomplished by cyanogen bromide than by any other method, a brominated cyanamide being formed in accordance with the preceding scheme.

The reaction between 1-phenylpiperidine and cyanogen bromide leads, after several hours, to the formation of *phenyl-ω-bromopiperidine cyanamide*,  $\text{CH}_3\text{Br} \cdot (\text{CH}_2)_4 \cdot \text{NPh} \cdot \text{CN}$ , and the quaternary bromide,  $\text{C}_5\text{NH}_{10}\text{PhBr} \cdot (\text{CH}_2)_4 \cdot \text{NPh} \cdot \text{CN}$ . The latter is a brown oil, which is identified by conversion into the *platinichloride*,  $(\text{C}_2\text{H}_5\text{N})_2\text{PtCl}_2$ , m. p. 121–122°. The former is an oil which is soluble in concentrated acids, and by prolonged boiling with 48% hydrobromic acid is changed into the oily *ω-bromoaniline hydrobromide*, from an aqueous solution of which the *picrate* is obtained as a yellowish green powder which sinters at 137° and has m. p. 141°. The *base* is a faintly coloured, feebly-smelling oil, which yields the *platinichloride*,



m. p. 117–118°, in reddish-yellow crystals, and by warming it is converted quantitatively to 1-phenylpiperidine hydrobromide, m. p. 235–236°. 1-Phenylpiperidine *picrate* has m. p. 148°.

Piperidine in excess and phenyl *ω*-bromoaniline cyanamide react to form *ω*-piperidinoaniline phenylcyanamide,  $\text{C}_6\text{H}_5\text{NH}_2 \cdot (\text{CH}_2)_4 \cdot \text{NPh} \cdot \text{CN}$ , b. p. 230–232°/9 mm., of which the *picrate*, m. p. 112°, forms yellow leaflets, and the *methiodide*, m. p. 101°, white leaflets.

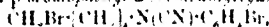
*Phenylmethylenepiperidinium iodide* has m. p. 146°; distillation of the hydroxide does not cause a rupture of the ring, but regenerates 1-phenylpiperidine.

1-*p*-Tolylpiperidine, prepared from *p*-toluidine and *ω*-bromopentane, has b. p. 268–269° (compare Löffmann and J. J. Abstr. 1891, 1244; Scholtz and Wassermann, this vol. i, 739) and behaves with cyanogen bromide in a similar manner to 1-phenylpiperidine. The *bromide*,  $\text{C}_7\text{H}_7 \cdot \text{C}_5\text{NH}_{10}\text{Br} \cdot (\text{CH}_2)_4 \cdot \text{N}(\text{C}_2\text{H}_5)_2 \cdot \text{CN}$ , m. p. 124–125°.

from 1,3-pyrazolone, white needles. *p*-Tolyl- $\omega$ -bromomethylcyanamide,  $\text{CH}_3\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_6\text{H}_4)\cdot\text{CN}$ , is an oil which reacts with an excess of *p*-toluidine to form *\omega*-*p*-toluidinoamyl *p*-tolylecyanamide,  $\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_6\text{H}_4)\cdot\text{CN}$ .

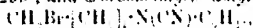
*m*. p. 71, the hydrochloride and hydrobromide of which have *m*. p. 153–54 and 149° respectively. The preceding cyanamide is hydrolysed with sulphuric acid, yielding *s*-di-*p*-tolylpentamethylenediamine,  $\text{C}_6\text{H}_4(\text{CH}_2)_5\text{NH}\cdot\text{C}_6\text{H}_4$ , *m*. p. 60, of which the hydrochloride, platinochloride, hydrobromide, and sulphate are mentioned; the dinitroso derivative is a yellow, crystalline powder, *m*. p. 70–71, which yields a triazine derivative by reduction. *P*-cyanodi-*p*-tolylpentamethylenediamine,  $\text{C}_6\text{H}_4(\text{CH}_2)_5\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4$ , prepared from the diamine and cyanogen bromide in ethereal solution, has *m*. p. 92°.

1,2-Diphenylpiperidine reacts somewhat slowly with cyanogen bromide and yields *p*-bromophenyl  $\omega$ -bromomethylcyanamide,



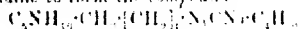
*m*. p. 51, which by boiling with sodium phenoxide in alcoholic solution forms the ether,  $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Br}$ , *m*. p. 60°, *b*. p. 275–280/10 mm.

1,3-Azylpiperidine and cyanogen bromide yield isomylpiperidine hydrobromide, *m*. p. 255, and  $\omega$ -bromomethylisomylcyanamide,



which reacts with piperidine to form  $\omega$ -piperidino-methylisomylcyanamide,  $\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_{11}$ , *b*. p. 213–215/12 mm., of which the picrate, platinochloride, methiodide, and methochloride are oils; the platinochloride of the last mentioned, however, forming red crystals, *m*. p. 143°, sintering at 137°. The preceding cyanamide is hydrolysed by heating with concentrated hydrochloric acid at 130° for fifteen to twenty hours, and yields  $\omega$ -piperidino-methylisomylamine,  $\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_{11}$ , *b*. p. 170–172/9 mm., of which the picrate has *m*. p. 152°.

1-Ethylpiperidine,  $\text{C}_6\text{H}_{11}\text{NH}\cdot\text{C}_2\text{H}_5$ , *b*. p. 175–176°, is obtained from butylamine and acetylbromopentane in 85–90% yield; the picrate has *m*. p. 15°. Butyl  $\omega$ -bromomethylcyanamide,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_{11}$ , reacts with piperidine to form the compound



*b*. p. 176–197/12 mm.

C. S.

**Compounds of Dichromates of Bivalent Metals with Organic Bases.** NICOLA PARRAYANO and A. PASTA (*Gazzetta*, 1907, 37, ii, 292–294). The normal dichromates of bivalent metals, when obtained, are unstable, but they yield with organic bases well defined addition compounds which are stable and can be prepared relatively easily.

The compounds prepared by the authors were obtained by adding the organic base to a solution containing potassium dichromate (1 mol.) and the neutral sulphate (1 mol.), or in the case of cadmium, the nitrate.

The copper dichromate-pyridine compound,  $\text{CuCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{NH}_2$ , forms a green, pulverulent precipitate and dissolves readily in ammonia, giving an intensely green liquid from which can be isolated: (1) the compound,  $\text{CuCr}_2\text{O}_7\cdot 4\text{NH}_3\cdot 2\text{H}_2\text{O}$ , in diamond, black, prismatic crystals, and (2) the compound,  $\text{CuCrO}_4\cdot 4\text{NH}_3$ , in small, green prisms; both these compounds

The copper dichromate compounds are as follows:

$\text{CuCr}_2\text{O}_7 \cdot 20\text{H}_2\text{O} \cdot (\text{NH}_4)_2$  crystallises from water in chestnut-red laminae.

The nickel dichromate pyridine compound,  $\text{NiCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ , forms pale chestnut prisms; the aniline compound,  $\text{NiCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , is a bright red, crystalline crust decomposable by water; the ethylenediamine compounds,  $\text{NiCr}_2\text{O}_7 \cdot 20\text{H}_2\text{O} \cdot (\text{NH}_2)_2$ , almost black crystals, and  $\text{NiCr}_2\text{O}_7 \cdot 3\text{C}_2\text{H}_4 \cdot (\text{NH}_2)_2$ , pale red crystals. The nickel chromate ethylenediamine compound,  $\text{NiCrO}_4 \cdot 3\text{C}_2\text{H}_4 \cdot (\text{NH}_2)_2$ , is extremely stable and forms small, dirty yellow prisms.

Cobalt dichromate forms the compounds:  $\text{CoCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ , minute, black crystals;  $\text{CoCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , minute, brick-red crystals, decomposable by water. The compound,  $\text{CoCrO}_4 \cdot 2\text{C}_2\text{H}_4 \cdot (\text{NH}_2)_2$ , forms silky, golden-yellow needles.

Cadmium dichromate gives:  $\text{CdCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ , forming a coarse, yellow, crystalline precipitate;  $\text{CdCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , as minute, yellow crystals decomposed by water;  $\text{CdCr}_2\text{O}_7 \cdot 3\text{C}_2\text{H}_4 \cdot (\text{NH}_2)_2$ , as minute, orange-yellow crystals.

Zinc dichromate forms:  $\text{ZnCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ , which resembles the corresponding cadmium compound, but is not altered by water;  $\text{ZnCr}_2\text{O}_7 \cdot 3\text{NH}_2\text{Ph} \cdot \text{H}_2\text{O}$ , which resembles the analogous aniline derivative in appearance and properties.

Manganese dichromate yields:  $\text{MnCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$ , and  $\text{MnCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$ , both forming dark chestnut crystals.

All these compounds are in accord with Werner's theory of coordination (*Zeitsch. anorg. Chem.*, 1893, 3, 267; Abstr., 1893, ii, 379).

The solubility of the pyridine derivatives of the dichromates increases, whilst the stability decreases, continuously in the series copper, nickel, cobalt, cadmium, zinc, manganese. The conductivity of these compounds increases in the order: nickel, cobalt, cadmium, zinc, manganese.

T. H. P.

**Diphenyldimethylhexamethyleneimine.** Guido Baccini (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 344—349; Compare Harries and de Osa, Abstr., 1903, i, 815).—Reduction of benzoylbenzoxime with aluminium amalgam yields: (1)  $\gamma$ -aminobenzophenone (Harries and de Osa, *loc. cit.*); (2) a substance, b.p. much above 238°, and (3) 4:5-diphenyl-2:7-dimethylhexamethyleneimine,  $\text{NH} < \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHPh}$  which is a colourless, mobile liquid, b.p. 235°—238°, with an odour recalling that of piperidine and forming strongly alkaline solutions. Its benzoyl derivative,  $\text{C}_{22}\text{H}_{21}\text{N}$ , crystallises from aqueous alcohol in white needles, m. p. 101—102°, and has the normal molecular weight in freezing benzene. The parent,  $\text{C}_{18}\text{H}_{19}\text{N}$ , crystallises from benzene or water in yellow needles, m. p. 143—144°; the oxalate crystallises from alcohol in saccharine scales, or from aqueous alcohol in slender needles, m. p.

113-115°

m. p. 154-155°

from water in small, white, glistening needles, soluble in water and the acids;  $C_{10}H_{11}N$ ,  $HANCl$ , crystalline from water in long yellow needles, m. p. 162-163°, and dissolves readily in alcohol.

T. M.

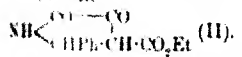
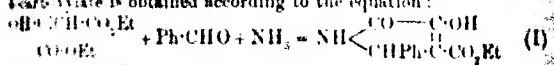
[Preparation of Isatin.] KALLÉ & CO. (D.R.-P. 184693, 184694)

Nitro-mandelic acid, when reduced with zinc dust in an alkaline aqueous solution containing ammonium chloride and the filtrate treated with excess of concentrated hydrochloric acid, furnishes a yellow crystalline product, m. p. 162°, which is probably an anhydride of  $\alpha$ -hydroxy- $\beta$ -aminomandelic acid,  $OH-NH-C_6H_4-CH(OH)-CO_2H$ , and may be represented by the formula  $C_6H_4 \begin{smallmatrix} C(OH)-CO_2H \\ \diagup \\ NH \end{smallmatrix}$ . When the anhydride is melted either alone or preferably with a dehydrating agent, such as acetic anhydride, it gives rise to isatin or acetylisatin respectively. Isatin is also produced when the anhydride is dissolved in aqueous sodium carbonate or hydroxide and the solution subsequently acidified.

G. T. M.

### Action of Ethyl Oxalacetate on Aldehydes in Presence of Ammonia and Primary Amines: a New General Reaction of Aldehydes. LOUIS J. SIMON AND A. CONDREU. (*Ann. Chim. Phys.* [6], 12, 5-58).

Ethyl oxalacetate readily condenses with aldehydes in presence of ammonia, forming derivatives of 2:3 diketopyrrolidine; thus, in the case of benzaldehyde, ethyl 2:3 diketo-5 phenylpyrrolidine-1-carboxylate is obtained according to the equation:



If a primary amine is used in place of ammonia, a compound containing the group NR instead of the NH of the pyrrolidine nucleus is obtained. Some of the substances obtained in this way have been described already (Abstr., 1904, i, 521 and 812; 1905, i, 887 and 888; this vol., 725). The following facts are new.

The diketopyrrolidine derivatives, as liberated from their ammonium salt by adding acid, contain  $1H_2O$ ; as this water is not present in the ammonium salts which are derived from the enolic formula (I) above, it is probably combined with the carbonyl group in position 3 in formula II, thus:  $NH \begin{smallmatrix} CO-C(OH)_2 \\ \diagup \quad \diagdown \\ CHPh-CH-CO_2Et \end{smallmatrix}$  (III). This water can be expelled by heating in a vacuum at  $100^\circ$ ; the anhydrous substance remaining sometimes takes up water again from the atmosphere (salicylic and piperonylic derivatives), but in other cases does not do so. The substance decomposing at  $185^\circ$ , obtained from benzaldehyde and previously given the formula I above (Abstr., 1904, i, 522), is really the hydrated substance (III); when dehydrated, it decomposes at the

same temperature, 185°. The ammonium salt,  $\text{NH} \begin{smallmatrix} \text{CO} & \text{CO} \\ | & | \\ \text{CH}(\text{C}_6\text{H}_5) & \text{CH}(\text{C}_6\text{H}_5) \end{smallmatrix} \text{CO}_2\text{Et}$ , decomposes at 175°; the analogous aniline salt melts at 160° and the piperidine salt decomposes at 173°; the last two substances, when heated at 120–130°, lose the whole of the combined base, leaving the anhydrous compound (I).

The ammonium salt,  $\text{NH} \begin{smallmatrix} \text{CO} & \text{CO} \\ | & | \\ \text{CH}(\text{C}_6\text{H}_4\text{OH}) & \text{CH}(\text{C}_6\text{H}_4\text{OH}) \end{smallmatrix} \text{CO}_2\text{Et}$ , of the compound from salicylaldehyde, ethyl oxalacetate and ammonia, decomposes at 190°; the copper salt crystallises with 4H<sub>2</sub>O. The ammonium salt of the compound from anisaldehyde decomposes at 175°. The compound  $\text{OH} \cdot \text{C}_6\text{H}_4(\text{OMe}) \cdot \text{CH} \begin{smallmatrix} \text{CO} \\ | \\ \text{CH}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{CO}$  prepared from vanillin crystallises in rhombic prisms with 2H<sub>2</sub>O; the ammonium salt decomposes at 175°. The compound from piperonal gives an anhydrous salt decomposing at 185°; the copper salt,  $(\text{C}_{11}\text{H}_{11}\text{NO}_4)_2\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , forms yellowish green needles.

Furfuraldehyde condenses with ethyl oxalacetate and ammonia to form the compound  $\text{C}_4\text{H}_3\text{O}_4 \cdot \text{CH} \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\ | \\ \text{CO} \cdot \text{CO} \end{smallmatrix}$ . From acetaldehyde

the compound  $\text{NH} \begin{smallmatrix} \text{CO} & \text{CO} \\ | & | \\ \text{CHMe} & \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$  (m. p. 146°) is obtained similarly; it is anhydrous and has a definite melting point, differing in these respects from all the other compounds of a similar type. A second form of this substance (m. p. 132°), also anhydrous, is probably one of the two compounds being probably the racemic and meso-isomers which should exist owing to the presence of two asymmetric carbon atoms. The copper salt crystallises with 1H<sub>2</sub>O.

The compound  $\text{NH} \begin{smallmatrix} \text{CO} & \text{CO} \\ | & | \\ \text{CH}(\text{C}_6\text{H}_{13}) & \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$  (m. p. 125°) prepared from heptaldehyde, ethyl oxalacetate, and ammonia, is also anhydrous, melts without decomposing, and appears to exist in the form of the ammonium salt, which decomposes at 146°; the potassium and base salts are crystalline.

*Ethyl 2:3-diketo-5-phenyl-1-methylpyrrolidine-4-carboxylate.*

$\text{NMe} \begin{smallmatrix} \text{CO} & \text{CO} \\ | & | \\ \text{CHPh} & \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$   
prepared from ethyl oxalacetate, benzaldehyde, and methylamine crystallises in white needles, is anhydrous, decomposes at 172°, and gives a crystalline methylamine salt,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}_2 \cdot \text{NH}_2\text{Me}$ , which decomposes at 155°.

*Ethyl 2:3-diketo-5-phenyl-1-allylpyrrolidine-4-carboxylate.*

$\text{N}(\text{C}_2\text{H}_5) \begin{smallmatrix} \text{CO} & \text{CO} \\ | & | \\ \text{CHPh} & \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$   
prepared similarly by using allylamine, crystallises from alcohol in slender needles, m. p. 146°; the allylamine salt forms sticky prisms and decomposes at 142°.

*Ethyl 2:3-diketo-5-phenyl-1-benzylpyrrolidine-4-carboxylate.* prepared

by using benzylideneaniline, the barium salt, m. p. 140°, is crystalline.

**Body 1: 3-diketo-1:5-diphenylpyrrolidine-4-carboxylate**, obtained from ethyl oxalacetate, benzaldehyde, and aniline (compare Abstr. 1934, 2, 512), is also formed when ethyl oxalacetate is left at the ordinary temperature in ethereal solution with benzylideneaniline. The potassium salt,  $C_{17}H_{15}O_4NK \cdot 3\frac{1}{2}H_2O$ , the barium, copper, and other salts are described; it does not form a salt with aniline.

In the introduction to the paper, the relationship of the substances described with compounds containing the same fundamental nucleus is discussed at length.

W. A. D.

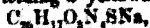
**2 and 4 Nitro 6-methyl a stilbazole.** FELIX B. AHRENS and LOUIS L. THERT (*Ber.*, 1907, 40, 3400—3406). **2 Nitro 6-methyl a stilbazole**,  $C_{14}H_{11}O_2N_2$ , obtained by heating o-nitrobenzaldehyde with ethylene and zinc chloride at 180—190° for ten hours, crystallises from 40% alcohol in slender, pale yellow needles, m. p. 55—57°. The following salts have been prepared: *hydrochloride*,  $C_{14}H_{11}O_2N_2 \cdot HCl$ , platy needles, m. p. 235—275° (decomp.); *hydrobromide*, slender, tabular plates, m. p. 240—241° (decomp.); *hydriodide*, yellow plates, m. p. 187—199°; *nitrate*, pale yellow needles, m. p. 148—149°; *acetate*,  $C_{14}H_{11}O_2N_2$ , m. p. 227—228° (decomp.) after sintering at 170°; *mercurichloride*,  $C_{14}H_{11}O_2N_2 \cdot HCl \cdot HgCl_2$ , m. p. 147—148°; *mercurisulphate*, m. p. 191—192°; *platinichloride*, yellow plates; *hydrogen sulphate*, yellow needles, m. p. 130—131°; *stannichloride*,  $C_{14}H_{11}O_2N_2 \cdot HCl \cdot SnCl_4$ , yellow needles, m. p. 225—226°;  $C_{14}H_{11}O_2N_2 \cdot HCl \cdot ZnCl_2$ , m. p. 175—176°;  $C_{14}H_{11}O_2N_2 \cdot HCl \cdot BaCl_2$ , long, yellow needles decomposing at 158°.

The isomeric **4 nitro 6-methyl a stilbazole** crystallises from dilute alcohol in long needles, m. p. 131—132°. The salts prepared are: *hydrochloride*,  $C_{14}H_{11}O_2N_2 \cdot HCl$ , long yellow needles, m. p. 221—222°; *nitrate*, pale yellow plates, m. p. 162—163°; *platinichloride*, decomposes at 155°; *aurichloride*, m. p. 225—226°; *mercurichloride*, yellow needles.

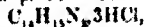
When reduced with tin and hydrochloric acid, the o-nitro-compound yields **2 o-amino 6-methyl a stilbazole**,  $C_{14}H_{11}N_2$ , in yellow, glistening needles, m. p. 136—137°. This readily absorbs carbon dioxide from the air, yielding the *carbonate*,  $(C_{14}H_{11}N_2)_2 \cdot H_2CO_3$ . The *hydrochloride*,  $C_{14}H_{11}N_2 \cdot HCl$ , crystallises in pale yellow plates, m. p. 234—235°; the *stannichloride*,  $C_{14}H_{11}N_2 \cdot 2HCl \cdot 2SnCl_4$ , forms orange-coloured needles, m. p. 278°, and the *mercurichloride*, similar needles, m. p. 164°. A *platinichloride* has not been obtained in a crystalline form. The reduced amino compound yields an *azo dye*,  $C_{14}H_{11}ON_2K$ , with an aqueous solution of  $\beta$ -naphthol; it crystallises from alcohol in red scales, m. p. 137—138°, and dyes wool or silk.

**4-Amino 5-methyl a stilbazole** forms pale brown needles, m. p. 134—140°. The *hydrochloride* decomposes at 265°; the *mercurichloride* crystallises in reddish brown needles, m. p. 260° (decomp.); the *stannichloride* forms brown needles, m. p. 188—189°. The *azo dye*,  $C_{14}H_{11}ON_2K$ ,

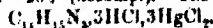
4-Amino-6-methyl-a-stilbazole couples with diazotised sulphanilic acid in alkaline solution yielding a yellowish-brown dye,



which is readily reduced to sulphathic acid and diamino-a-stilbazole,  $C_{11}H_{13}N_2$ , the latter of which crystallises from alcohol in long needles, m. p. 148—149°. The hydrochloride,



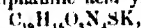
forms needles, m. p. 249—250° (decomp.). The mercurichloride,



crystallises in yellow needles, m. p. 179—180°; the stannichloride forms glistening yellowish-brown needles, m. p. 245—246° (decomp.).

The bisdiazio-derivative of the base complex with an excess of  $\beta$ -naphthol yielding a pale red dye,  $C_{22}H_{21}O_2N_4S$ , which crystallises from alcohol in plates, m. p. 180—181°. With diazotised sulphonic acid (R-acid), a brownish red dye,  $C_{21}H_{21}O_2N_4S_2$ , is obtained; it crystallises from water in plates.

4-Amino-6-methyl-a-stilbazole yields a dye,  $C_{20}H_{19}O_2N_2SN_2$ , with diazotised sulphanilic acid; it crystallises from alcohol in yellowish-brown plates, and dyes silk, wool, and cotton yellow. 4-Amino-a-stilbazole and diazotised sulphanilic acid yield a yellow dye,



which can be reduced to sulphathic acid and diamino-a-stilbazole,



the latter of which crystallises in long, yellow needles, m. p. 156—157°. Its hydrochloride,  $C_{11}H_{13}N_2 \cdot 3HCl$ , forms yellowish-red diamine needles; its mercurichloride, red needles, and its stannichloride, long needles, m. p. 240—241°.

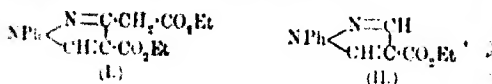
**New Process for the Preparation of Aromatic 3-Hydroxy-6-pyrazolones or Pyrazolidones.** AUGUST MICHAELIS and KARL SCHENK (*Ber.*, 1907, 40, 3568—3569).—Malonic acid and acetyl-phenylhydrazine condense in presence of phosphorus trichloride to 3-hydroxy-1-phenyl-5-pyrazolone previously described by Michael and Burmeister (*Abstr.*, 1892, 1904). In a similar manner malonic acid condenses to 3-hydroxy-1-phenyl-4:4-dimethyl-5-pyrazolone,  $NPh \cdot C \begin{smallmatrix} CO \cdot CMe_2 \\ \diagup \quad \diagdown \\ N = C \cdot OH \end{smallmatrix}$ , separating in colourless crystals, m. p. 178°.

Similarly, acetyl *p*-bromophenylhydrazine and malonic acid condense to 3-hydroxy-1-*p*-bromophenyl-5-pyrazolone, crystallising in plates, m. p. 217°, and forming a red condensation product with benzaldehyde. The method appears to be generally applicable. E. F. A.

**Thionpyrazolones.** RICHARD STOERMER and D. JOHANNSEN (*Ber.*, 1907, 40, 3701—3703). The action of phosphorus pentasulphide on pyrazolones yields thionpyrazolones and is therefore analogous to that on pyrrolidone (compare Tafel and Lawaczeck, this vol., 4, 77). The pyrazolone, obtained from ethyl dimethylacetacetal, on

is long, yellow prisms, m. p. 45—45°, b. p. 187—190°/15 mm.  
 yields a dimethiodide, m. p. 210—215°, which with  
 yields a methochloride, the platinumchloride of which has  
 1-phenyl-3-methyl-4:4-diethyl-5-thionpyrazolone,  $C_{11}H_{15}N_2S$ ,  
 m. p. 80°, and 1-phenyl-3-methyl-5-thionpyrazolone,  $C_{10}H_{13}N_2S$ ,  
 m. p. 100°, are best prepared in xylene solution.

**Action of Phenylhydrazine on Ethyl Formylglutaconate.**  
 F. WISLICKUS and KARL BAHRT (*Annalen*, 1907, 356, 32—41).  
 The action of phenylhydrazine on ethyl formylglutaconate has been  
 studied with the object of throwing light on certain points in  
 the reaction left indefinite by the investigations of Wislitzky and  
 Hesse (Abstr., 1901, i, 361) and Hesse (*Diss.*, Würzburg, 1903).  
 The first product of the reaction is now found to be an additive com-  
 pound,  $NPh \cdot NH \cdot CH(CH_2 \cdot CO_2Et) \cdot CH(CO_2Et) \cdot CHO$  or  
 $NPh \cdot NH \cdot CH(CH_2 \cdot CO_2Et) \cdot C(CO_2Et)CH \cdot OH$ .  
 This condenses, forming ethyl 1-phenylpyrazole-3-acetate-4-carboxylate  
 (I) or ethyl 1-phenylpyrazole-4-carboxylate (II), depending on the  
 conditions. The latter product is formed when the additive compound  
 is heated in absence of air, which explains its formation on distillation  
 of ethyl formylacetate-phenylhydrazine (*loc. cit.*):



The additive compound,  $C_{18}H_{27}O_4N_2$ , formed by mixing ethyl  
 formylglutaconate and phenylhydrazine in cold ethereal solution  
 crystallizes in needles, m. p. 70°, and on exposure to air in etheral  
 solution forms ethyl 1-phenylpyrazole-3-acetate-4-carboxylate, m.  
 p. 96°. 1-Phenylpyrazole-3-acetate-4-carboxylic acid,  $C_{17}H_{15}O_4N_2$ ,  
 m. p. 221°, is formed by boiling the ester with aqueous barytes,  
 gives carbon dioxide on prolonged heating at 140°, forming 1-phenyl-  
 methylpyrazole-4-carboxylic acid, and yields the ester, m. p.  
 96°, when boiled with alcoholic hydrogen chloride. The barium,  
 $H_2O, N_2, Ba, CH_3O$ , and silver,  $C_{17}H_{15}O_4N_2, Ag_2$ , salts were analysed.  
 When heated at 60—70° in presence of air, the additive compound  
 yields a mixture of the above ester and ethyl 1-phenylpyrazole-  
 4-carboxylate, m. p. 96—97°, together with ethyl acetate. In the  
 absence of air, ethyl 1-phenylpyrazole-4-carboxylate and ethyl acetate  
 are formed.  
 When p-bromophenylhydrazine is added to an ethereal solution of  
 ethyl formylglutaconate, the additive compound does not separate, but  
 at some time the solution deposits ethyl 1-p-bromophenylpyrazole-  
 3-acetate-4-carboxylate,  $C_{18}H_{17}O_4N_2Br$ , m. p. 128—129°, which does not  
 react with potassium dichromate in concentrated sulphuric



the additive compound separates, and if heated in a current of carbon dioxide, loses water and ethyl acetate forming ethyl 1-*p*-bromophenylpyrazole-4-carboxylate,  $C_{12}H_{11}O_2N_2Br$ , which crystallises in needles, m. p. 133—134°.

G. I. Y.

**The Hydrazones of Ethyl Formylacetate.** WILHELM WISLIZENUS and H. W. BYWATERS (*Annalen*, 1907, 356, 45—50).—From preceding abstract; Wislizenus and Bindemann, *Abstr.*, 1907, 251.—The phenylhydrazone of ethyl formylacetate yields the same condensation products as are obtained from the additive compound of phenylhydrazine and ethyl formylglutamate.

Ethyl 1-phenylpyrazole-3-acetate-4-carboxylate is formed when the phenylhydrazone is treated with hydrogen chloride in concentrated alcoholic solution, whilst ethyl 1-phenylpyrazole-4-carboxylate is obtained on distillation of the phenylhydrazone.

The *p*-bromophenylhydrazone of ethyl formylacetate,  $C_{12}H_{11}O_2N_2Br$ , crystallises in slightly yellow prisms, m. p. 80—81°, is more soluble than the corresponding phenylhydrazone, and gives a black-red coloration with concentrated sulphuric acid, or a brown coloration with alcoholic ferric chloride. On treatment with hydrogen chloride in absolute alcoholic solution, it condenses, forming ethyl 1-*p*-bromophenylpyrazole-3-acetate-4-carboxylate (preceding abstract), and distils in a vacuum with partial decomposition, and gives a pyrazolone reaction after reduction. 1-*p*-Bromophenylpyrazole-3-acetate-4-carboxylic acid,  $C_{12}H_9O_4N_2Br$ , crystallises in colourless needles, m. p. 229—230°; the silver salt, m. p. 270° (decomp.). When distilled in a vacuum, the *p*-bromophenylhydrazone of ethyl formylacetate and ethyl 1-*p*-bromophenylpyrazole-4-carboxylate, m. p. 131—132°.

The semicarbazone of ethyl formylacetate,  $C_6H_{11}O_3N_3$ , crystallises in almost colourless prisms, m. p. 147—148°, and when heated at 170° in a sealed tube decomposes, forming alcohol, hydrazine-carbonic acid and a resin, which is soluble in alcohol and forms a silver salt.

G. I. Y.

**Preparation of a *p*-Aminodiphenylaminesulphonic Acid.** KARL ERMANN (*D.R. P.* 181179).—Although diphenylamine does not easily convert into a monosulphonic acid, one sulphonic group readily introduced into the molecule of *p*-aminodiphenylamine, providing that the sulphuric acid contains a certain proportion of peroxide and that the sulphonation is effected at about 110—120° temperature required being dependent on the amount of peroxide present. The time required to complete the reaction varies from a few minutes to three hours. *p*-Aminodiphenylaminesulphonic acid, which is formed by dissolving in alkali and reprecipitating by mineral acids, is soluble in hot water, and crystallises from this solvent in colourless needles. Its sodium and potassium salts crystallise from water and the diazo derivative separates as a yellow, crystalline product. The acid differs from its isomerides in the coloration it forms with chromic acid and ferric chloride.

G. I. Y.

**Preparation.** **Acetic Anhydride for Aniline.** (R. P. 163785).—The direct sulphonation of tetramethylenediamine does not lead readily to the formation of a monosulphonic acid. The product is contaminated by coloured by-products of the sulphone type. It has now been found that the monosulphonic acids of this series may be synthesized by the condensing formaldehyde with dimethyl- or diethyl-amine and dimethylamine *m*-sulphonic acid.

**Tetramethylenediaminodiphenylmethane *m*-sulphonic acid,**  
 $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{SO}_3\text{H},$   
 crystallises from aqueous solutions, and its sodium salt may be salted out in the form of slender needles.

**Dimethylaminodithylaminodiphenylmethane *m*-sulphonic acid,**  
 $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{SO}_3\text{H},$   
 resembles its lower homologue. G. T. M.

**Action of Hydrazine Hydrate on Nitro compounds. I.** (R. P. 163785) (*J. pr. Chem.*, 1907, [ii], 70, 233–237).—A short account of the chief results of the study of the action of hydrazine hydrate on nitro compounds, previously unpublished or published only in dissertations.

Baerger showed (Abstr., 1893, i, 701) that whilst the action of hydrazine hydrate on oximes leads to substitution, *p*-nitrobenzene, nitrosodimethylaniline, and diphenylnitrosamine are reduced by hydrazine hydrate forming aniline, *p*-aminodimethylaniline, and *az*-diphenylhydrazine respectively. It has since been found that the action of hydrazine hydrate on *p*-nitrosodimethylaniline leads also to the formation of traces of dimethylamine, whilst if the action is moderated by addition of the hydrazine hydrate, tetramethyldiaminoazoxybenzene is formed.

Hallenbach (*Dis.*, Heidelberg, 1902), who obtained *o* and *p*-aminobenzoic acids by reduction of the nitrophenols with hydrazine hydrate, was unable to reduce *m*- or *p*-nitrobenzoic acid in this manner, and found that *m*-dinitrobenzene is reduced only to *m*-nitroaminobenzene. On the other hand, Hoesch (*Dis.*, Heidelberg, 1904) has obtained

**azobenzophthalhydrazide,**  $\text{NH}_2\begin{array}{c} \diagup \text{CO}\cdot\text{NH} \\ \diagdown \text{CO}\cdot\text{NH} \end{array}$  by reduction of ethyl azobenzophthalate by means of hydrazine hydrate.

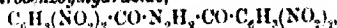
The action of hydrazine hydrate on ethyl 3:5-dinitrobenzoate (Hallenbach *Dis.*, Heidelberg, 1902; see following abstract) leads to the formation of 3:5-dinitrobenzophthalhydrazide, which is reduced by an excess of hydrazine hydrate forming 3-nitro-5-aminobenzophthalhydrazide. Similarly, 3-dinitrobenzoic acid forms the hydrazine salts of 3:5-dinitro- and nitro-5-amino benzoic acids. The second nitro group, as in the case of *m*-dinitrobenzene, cannot be reduced in this manner.

Hallenbach (*loc. cit.*) found that 2:4-dinitrobenzoic acid reacts in analogous manner to hydrazine hydrate, forming 2-nitro-4-aminobenzophthalhydrazide. 2:4-Dinitrophenylhydrazine, on the contrary, is not reduced by hydrazine hydrate, which functions merely as an alkali, the reaction lead-

### Action of Hydrazine Hydrate on Nitro-compounds

**Action of Hydrazine Hydrate on Ethyl 3:5-Dinitrobenzoate.**—**WILHELM CURTIUS** and **ADOLF RIEDEL** (*J. pr. Chem.*, 1907, [ii] 1, 263). Compare preceding abstract).—3:5-Dinitrobenzoic acid,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{COOH}$ , prepared in a 63.7—69% yield by boiling ethyl 3:5-dinitrobenzoate with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellow, prismatic needles, m. p. 100°, reduces ammoniacal silver nitrate and Fehling's solutions when heated, and forms crystalline condensation products with aldehydes and ketones. The crystalline sodium derivative,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{COONa} \cdot \text{NH}_2$ , is analysed. The benzylidene derivative,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CH}(\text{Ph})_2$ , crystallises in slightly brown needles, m. p. 262°. The propylidene derivative,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CH}(\text{CMe}_2)_2$ , forms slightly yellow needles, m. p. 215.5°. The benzyl derivative,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CH}(\text{Ph})\text{NHAc}$ , crystallises in yellowish white needles, m. p. 201.5°. When treated with sodium nitrite in acetic acid solution, the hydrazide forms 3:5-dinitrobenzoyl azoimide,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CO} \cdot \text{N}=\text{N}$ , which is obtained in small, white crystals, fuses slightly when heated, and yields 3:5-dinitrobenzoic acid when boiled with aqueous sodium hydroxide. 3:5-Dinitrobenzoyl azoimide,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CO} \cdot \text{N}=\text{N}$ , formed by boiling the azoimide with aniline, crystallises in brown needles, m. p. 234°. Ethyl 3:5-dinitrophenylcarbamate,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NH} \cdot \text{CO}_2\text{Et}$  (I), prepared by boiling the azoimide in absolute alcohol, is obtained as a viscous, red oil, which yields 3:5-dinitroaniline when boiled with concentrated hydrochloric acid. 3:5-Dinitroacetanilide,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NH} \cdot \text{CO}_2\text{Et}$ , crystallises in yellowish-white needles, m. p. 191°. The action of boiling methyl alcohol on the azoimide leads to the formation of methyl 3:5-dinitrobenzoate and azobis-3:5-dinitrophenylcarbamide, m. p. 265°, formed together with 3:5-dinitroaniline by boiling 3:5-dinitrobenzoyl azoimide with water. It is probably identical with Struve and Radenhausen's tetranitrobenzoyl azoimide (*Ann.*, 1896, i, 35).

### Bis-3:5-dinitrobenzoylhydrazide,



prepared by the action of iodine on 3:5-dinitrobenzoylhydrazide in alcoholic solution, is obtained in a 30% yield as a yellow powder, m. p. 276°, and dissolves unchanged in concentrated sulphuric acid, being reprecipitated on addition of water. When heated in alcoholic hydrogen chloride at 100° in a sealed tube, it is decomposed into m-dinitrobenzene and hydrazine. The crystalline diacid derivative,  $\text{N}_2\text{H}_4(\text{CO} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2)_2$ , is described.

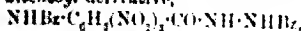
**Nitro-5-aminobenzoylhydrazide**,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2\text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , is obtained in a 60% yield together with a reddish-grey, crystalline solid, m. p. 283—284°, having the composition of bis-3:5-dinitrobenzoylhydrazide, when ethyl 3:5-dinitrobenzoate is boiled in concentrated alcoholic solution with an excess of hydrazine hydrate. 3:5-Di-

crystallizes in yellowish-brown needles, m. p. 221°. It reduces silver nitrate and Fehling's solutions when heated.

**Hydrazonium 3:5-dinitrobenzoate**,  $C_6H_3(NO_2)_2 \cdot CO_2 \cdot H_2N \cdot NH_2$ , prepared by heating 3:5-dinitrobenzoic acid with a limited amount of hydrazine hydrate in alcoholic solution, crystallizes in yellowish-brown needles, m. p. 168°, reduces ammoniacal silver nitrate and Fehling's solution in the cold, yields benzaldazine and 3:5-dinitrobenzoic acid when shaken with benzaldehyde in aqueous solution, and is converted to ethyl 3:5-dinitrobenzoate when heated with alcoholic hydrogen cyanide.

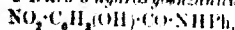
**Hydrazonium 3-nitro-5-aminobenzoate**,  $NH_2 \cdot C_6H_3(NO_2) \cdot CO_2 \cdot H_2N \cdot NH_2$ , prepared by boiling 3:5-dinitrobenzoic acid or its hydraxonium salt with an excess of hydrazine hydrate in alcoholic solution, crystallizes in reddish-yellow needles, m. p. 207° (decomp.), reduces ammoniacal silver nitrate and Fehling's solutions in the cold, and when shaken with benzaldehyde yields benzaldazine and 3-nitro-5-aminobenzoic acid.

The following substances derived from 3-nitro-5-aminobenzoic acid and hydrazine are described. The **hydrochloride**,  $C_6H_4(O_2N) \cdot NH \cdot CO_2 \cdot NH_2 \cdot 2HCl$ , crystallizes in m. p. 221–222°. The **benzylidene derivative**,  $C_{11}H_{11}O_2N_3$ , yellow, prismatic needles, m. p. 247–248°. The **m-hydroxybenzylidene derivative**,  $C_{11}H_{11}O_3N_3$ , reddish-brown leaflets, m. p. 242°. The **m-benzylidene derivative**,  $C_{11}H_{11}O_2N_3$ , yellow needles, m. p. 240°. The **propylidene derivative**,  $C_{10}H_{11}O_2N_3$ , golden needles, m. p. 208°. The **acetyl derivative**,  $NHAc \cdot C_6H_3(NO_2) \cdot CO \cdot NHAc$ , yellow needles, m. p. 256°. The **dibenzoyl derivative**,



slightly brown needles, m. p. 236°.

**3-Nitro-5-hydroxybenzoylazouimide**,  $NO_2 \cdot C_6H_3(OH) \cdot CO \cdot N=N$ , prepared by the action of sodium nitrite on 3-nitro-5-aminobenzoylhydrazide in aqueous solution, is obtained as a reddish-yellow, flocculent substance which becomes brown when dried in a desiccator and detonates when heated. It dissolves in aqueous sodium hydroxide with slight evolution of gas, forming a dark red solution, and on addition of sulphuric acid yields azouimide. **3-Nitro-5-hydroxybenzamide**,



formed by boiling the azouimide with aniline, crystallizes in white needles, m. p. 232°. The **urethane**,  $NO_2 \cdot C_6H_3(OH) \cdot NH \cdot CO_2Et$ , formed by heating the azouimide with absolute alcohol, is obtained as a viscous red oil, and, when heated with sodium hydroxide and hydrogen chloride successively, yields 3-nitro-5-aminophenol.

When heated with water, 3-nitro-5-hydroxybenzoylazouimide forms **3-nitro-5-hydroxyphenylcarbamide**,  $CO[NH \cdot C_6H_3(OH) \cdot NO_2]$ , and small amounts of 3-nitro-5-aminophenol. The carbamide is obtained as a brittle mass, decomp. 260–270°, and is decomposed by boiling concentrated sodium hydroxide forming 3-nitro-5-aminophenol.

**3-Nitro-5-aminobenzoylhydrazide**,  $N_2H_4[CO \cdot C_6H_3(NH_2) \cdot NO_2]$ , prepared by boiling 3-nitro-5-aminobenzoylhydrazide with iodine in alcoholic solution, is obtained as a yellow, granular powder, m. p. 243–264°, and is hydrolysed, forming hydrazine, by alcoholic hydrogen chloride at 100°.

Preparation of 5:5-Dialkylbarbituric Acids. J. M. M. (D.R.-P. 183857).—The ethyl dialkylmalonates are obtained by heating the dialkylmalonyldiurethanes produced from the dialkylmalonyl chlorides and alkylurethanes, either alone or in the presence of carbamide, phenyl carbonate, or a similar compound. G. I. M.

Preparation of 5:5-Dialkylbarbituric Acids. J. M. M. (D.R.-P. 183857).—The ethyl dialkylmalonates yield 5:5-dialkylbarbituric acids when heated either with biuret or an alkyl isophthate. Ethyl dialkylmalonates, when heated with either biuret or ethyl allophanate in alcoholic sodium ethoxide, furnish 5:5-dialkylbarbituric acids (compare Abstr., 1906, i, 461). G. I. M.

Preparation of 4:6-Dioxy-2-thio-5:5-dialkylpyrimidines. EMANUEL MERRICK (D.R.-P. 182764).—4:6-Dioxy-2-thio-5:5-diethylpyrimidine may be produced by heating diethyl malonate chloride with thiocarbamide at 100°, and 4:6-dioxy-2-thio-5:5-dipropylpyrimidine is similarly prepared from dipropylmalonyl chloride. These substances are readily oxidised to the corresponding 5:5-dialkylbarbituric acids by dilute nitric acid or alkaline permanganate. G. I. M.

Pyrimidines. XXIII. Uracil 4-carboxylic Acid. HENRI WHELER (Amer. Chem. J., 1907, 38, 358—366).—By the condensation of carbamide with ethyl oxalacetate, Müller (Abstr., 1877, i, 549) obtained a compound which he regarded as ethyl uracil 4-carboxylate,  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$ .

As no evidence was adduced to prove that the substance had the pyrimidine structure, it seemed possible that it might be the ester of the acid,  $\text{CO} \begin{smallmatrix} \diagup \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \diagdown \text{NH} \cdot \text{CO} \end{smallmatrix}$ , obtained by Gabriel (Abstr., 1886, i, 636) by the action of bromine on malyureide. Müller's ester has therefore been prepared and studied, and it has been found that on hydrolysis it yields an acid, which is not identical with Gabriel's acid, and on treatment with bromine is converted into dibromomaleic acid. It is proved, therefore, that Müller's ester has the structure originally assigned to it, that Gabriel was right in concluding that his acid was not a pyrimidine, and that malyureide has the constitution,  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$  proposed by Guareschi (Abstr., 1877, i, 458), and not  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H}$ , as suggested by Grimaux (Abstr., 1875, 752).

Uracil-4-carboxylic acid,  $\text{NH} \begin{smallmatrix} \diagup \text{CO} \cdot \text{NH} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , H<sub>2</sub>O, m. p. 347° (decomp.), crystallises from water in prisms; the methyl ester, m. p. 230°, forms colourless needles; the potassium and barium salts are described.

As a mixture of an additive compound,  $C_{11}H_{11}O_2N_2S$ , m. p. 132—133°, which crystallises in colourless needles and when boiled with hydrochloric acid yields a substance, m. p. 206—207°, which contains sulphur and no nitrogen. When ethyl cyanoacetylacetate is treated in the same way, an additive compound,  $C_{16}H_{17}O_3N_2S$ , m. p. 159°, is produced which separates from alcohol in colourless, flat prisms. Ethyl cyanoacetate, under similar conditions, yields an additive compound,  $C_{11}H_{13}O_3N_2S$ , m. p. 181° (decomp.), which crystallises from alcohol in colourless scales.

E. G.

Properties of Substituted Amidines.] BADISCHE ANILIN- und FARBEN (D.R.P. 180126).—The amidines derived from the aromatic orthodiamines may be employed as substitutes for camphor in the production of celluloid.

Methylbenzimidazole, m. p. 113—115°, trichloro 2-methyl-1-ethylbenzimidazole, m. p. 116—117° (from ethyl aceto-*o*-nitrotrichloroacetate), and 4:5:7-trichloro-1:2-dimethylbenzimidazole, m. p. 120—121°, can be worked up with nitrocellulose in the presence of alcohol.

G. T. M.

3-Amino-2-methylquinoline. O. STARK (*Ber.*, 1907, 40, 125—143).—When the oxime of 3-acetyl-2-methylquinoline is treated with sulphuric acid at 180°, the Beckmann reaction occurs, followed by hydrolysis, and the elimination of the acetyl group, and the final product is 3-amino-2-methylquinoline:  $C_9NH_7Me.CMe.NOH \rightarrow C_9NH_7Me.NH.COMe \rightarrow C_9NH_7Me.NH_2$ .

A 2% yield of 3-acetyl-2-methylquinoline may be obtained by treating an alcoholic solution of *o*-aminobenzaldehyde and acetylacetone with a few drops of piperidine. It melts at 78—79° (compare Zaslberg and Friedländer, *Abstr.*, 1892, 1106). The semicarbazone,  $C_{12}H_{13}N_3$ , crystallises from alcohol in small, colourless needles, m. p. 108°.

3-Amino-2-methylquinoline crystallises from ether in long, yellow needles, m. p. 159—160°, or from light petroleum in brilliant golden needles. The hydrochloride,  $C_{10}H_{11}N_2 \cdot 2HCl$ , obtained by passing dry hydrogen chloride into an absolute ethereal solution of the base, is a yellowish white, crystalline powder; the platinumchloride,  $C_{10}H_{11}N_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , forms glistening golden needles, and darkens on heating to 220—230°; the picrate,  $C_{10}H_{11}N_2 \cdot C_6H_3O_7N_3$ , also forms golden needles, and decomposes at about 235°. The acetyl derivative,  $C_{11}H_{12}N_2$ , crystallises from ether in needles, m. p. 56°. The solutions of the acetyl derivative do not fluoresce until hydrolysis has begun. The same acetyl derivative may also be obtained by the action of a phosphorus oxychloride solution of phosphorus pentachloride on the oxime.

When oxidised with permanganate, the aminomethylquinoline yields anthranilic acid. 4-Hydroxy-2-methylquinoline crystallises from

... yields quinaldine (2-methylquinoline), and ...  
 ... as stated by Conrad, Lämpach, and Kohnert (Abstr., 1911).

**Fluorescence of 3-Amino-2-methylquinoline and 8-Amino-2-hydroxy-2-methylquinoline. Use of 8-Amino-2-methylquinoline as an Indicator.** O. STARK (Ber., 1907, 40, 2436). Aqueous solutions of 3-amino-2-methylquinoline and 8-amino-2-hydroxy-2-methylquinoline do not fluoresce even in very dilute solutions. The former compound fluoresces in acid solution, and the latter in both acid and alkaline solution, thus indicating a relationship between fluorescence and dissociation. A pure solution of the hydroxy-derivative is best obtained by distillation in steam; it is then non-fluorescent, but the addition of a small trace of acid on alkali produces fluorescence.

8-Amino-2-methylquinoline is an excellent indicator in volumetric analysis and can replace methyl-orange. An alcoholic solution is the best.

**Some Metbinezammonium Dyes.** A. PORAI-KOSCHITZ [with P. SOLODOWNIKOFF and M. TROITZKI] (Zeitch. Farb. Ind., 1906, 13, 291—295. Compare Rupe and Porai-Koschitz, Abstr., 1906, 1, 514; Kölling and Witte, *ibid.*, 886).—2-m-Aminostyryl-6-methylquinoline,  $C_9H_8Me \cdot CH=CH \cdot C_6H_4 \cdot NH_2$ , prepared by reducing with stannous chloride and hydrochloric acid the corresponding nitro-compound prepared from *m*-nitrobenzaldehyde and 2:6-dimethylquinoline (Gask, Abstr., 1906, i, 41), crystallises from benzene in slightly yellow needles, m. p. 160.5°, and gives a yellow hydrochloride,  $C_{10}H_{16}N_2 \cdot HCl$ .

2-p-Nitrostyryl-6-methylquinoline,  $C_9H_8Me \cdot CH=CH \cdot C_6H_4 \cdot NO_2$ , prepared by condensing *p*-nitrobenzaldehyde with 2:6-dimethylquinoline, crystallises from pyridine as a bright green powder, m. p. 177°; reduction gives 2-p-aminostyryl-6-methylquinoline, which crystallises from dilute alcohol in bright yellow leaflets, m. p. 173°; melting at 164°; the hydrochloride,  $C_{10}H_{16}N_2 \cdot HCl$ , is purple and the benzoyl derivative forms an orange, crystalline powder, m. p. 224°.

2-p-Dimethylaminostyryl-6-methylquinoline,  $C_{10}H_{16}MeN \cdot CH=CH \cdot C_6H_4 \cdot NMe_2$ , obtained from *p*-dimethylaminobenzaldehyde and 2:6-dimethylquinoline, crystallises from dilute alcohol or pyridine in bright yellow needles, m. p. 198°; the hydrochloride,  $C_{20}H_{20}N_2 \cdot HCl$ , is a purple crystalline powder.

2-m-Aminostyrylacridine,  $C_{12}H_8 \cdot NH_2 \cdot CH=CH \cdot C_6H_4 \cdot NH_2$ , prepared by reducing 5-m-nitro-styrylacridine (Friedlander, Abstr., 1905, i, 391) with stannous chloride and hydrochloric acid, crystallises in short, yellow needles, m. p. 232—234°; its salts are red.

2-m-Aminostyrylacridine, prepared by heating *p*-nitro-benzaldehyde





5:7-Dibromo-3-ethylaminoisatin,  $C_{10}H_8ON_2Br_2$ , prepared by treating isatin with four times its weight of 85% alcoholic ethylamine solution, separates from ethyl acetate in white crystals and readily decomposes, losing ethylamine, in solution.

5-Bromo-3-ethylaminoisatin,  $C_{10}H_8ON_2Br$ , forms yellow crystals and melts at about  $167^\circ$ , forming a violet mass; the potassium derivative,  $C_{10}H_7ON_2BrK$ , crystallises in red needles.

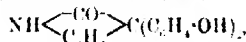
5:7-Dibromo-3-ethylaminoisatin,  $C_{10}H_8ON_2Br_2$ , is yellow, and decomposes about  $175^\circ$ .

5:7-Dibromo-3:3-diethylamino-1-ethyl- $\psi$ -isatin,  $C_{14}H_{14}ON_2Br_2$ , forms white needles, and is stable towards solvents.

5:7-Dibromo-2-ethylaminoisatin (5:7-dibromo-2-ethylaminoisatin),  $O_6H_4\langle\begin{smallmatrix} N \\ CO \end{smallmatrix}\rangle C \cdot NHEt$  or  $C_6H_4\langle\begin{smallmatrix} NH \\ CO \end{smallmatrix}\rangle CNEt$ , prepared by prolonged action of an excess of ethylamine on dibromoisatin, forms green crystals.

Dichloroisatin yields the three corresponding derivatives with ethylamine.

**Oxidation of Phenolisatin.** CARL LIEBERMANN and N. LUDWIG (*Ber.*, 1907, 40, 3588—3597).—In connexion with the study of indigotin-like colouring matters from isatin (this vol. i, 655), the authors have investigated the constitution of the dye formed by oxidation of phenolisatin. Baeyer and LAZARUS (*Abstr.*, 1880, 13) showed phenolisatin to have the constitution



and considered the deep red dye formed by oxidation of this with potassium ferricyanide in alkaline solution to be aminobenzaurin.

$NH_2 \cdot C_6H_4 \cdot C(C_6H_4 \cdot OH)\langle\begin{smallmatrix} CO \\ C_6H_4 \end{smallmatrix}\rangle$ . It is found now that the dye is

2-aminoaurin,  $NH_2 \cdot C_6H_3(OH) \cdot C(C_6H_4 \cdot OH)\langle\begin{smallmatrix} CO \\ C_6H_4 \end{smallmatrix}\rangle$ , only traces of aminobenzaurin being formed.

The name diphenolisatin is to be preferred to phenobenzaurin in agreement with the constitution. Diphenolisatin, m. p. 260—261° (230°: Baeyer and LAZARUS, *loc. cit.*), forms stable compounds with ether, m. p. 70—80°, and chloroform, decomp.  $110^\circ$ . Contrary to Baeyer and LAZARUS' statement, diphenolisatin forms a triacetate,  $C_{26}H_{18}O_9Na_3$ , which separates from alcohol in white, microscopic crystals, m. p. 201—202°.

Halogenated diphenolisatins are prepared from halogenated isatin in the same manner as diphenolisatin from isatin. *Bromodiphenolisatin*,  $NH\langle\begin{smallmatrix} CO \\ C_6H_3Br \end{smallmatrix}\rangle C(C_6H_4 \cdot OH)_2$ , crystallises in white needles,

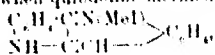
m. p. 335—336°, and forms a triacetate,  $C_{25}H_{17}O_9NBrAc_3$ , m. p. 217°.

*Dibromodiphenolisatin*,  $NH\langle\begin{smallmatrix} CO \\ C_6H_2Br_2 \end{smallmatrix}\rangle C(C_6H_4 \cdot OH)_2$ , forms a triacetate,  $C_{24}H_{15}O_9NBr_2Ac_3$ , m. p. 237—238°. *Chlorodiphenolisatin*, m. p. 237—238°. *Dichlorodiphenolisatin*, m. p. 276—277°.

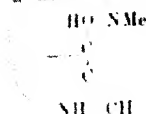
... is alkaline solution by potassium persulfate. The action of iodine on diphenolisation in alkaline solution leads to the formation of a blue colour. The aminoaurins are obtained in colourless amorphous powders, insoluble in water or benzene, but readily soluble in acid alcohol or glacial acetic acid; the absorption bands in the spectra of the cherry-red, alkaline solutions lie nearer to the D than those in the aurin spectrum. The coloration with concentrated sulphuric acid is redder with aminoaurin than with aurin.

The following aminoaurins have been analysed: 2-aminoaurin,  $C_{19}H_{14}O_5N$ ; 5-bromo-2-aminoaurin,  $C_{19}H_{13}O_5NBr$ ; 3,4-dibromo-2-aminoaurin,  $C_{19}H_{11}O_5NBr_2$ ; 5-chloro-2-aminoaurin,  $C_{19}H_{13}O_5NCl$ ; dichloro-2-aminoaurin,  $C_{19}H_{11}O_5NCl_2$ . G. Y.

**Methylquindolanol.** FRIEDRICH FICHTER and HANS PROMER (*Ber.*, 1907, 40, 3478).—It was shown by Fichter and Boebring (this vol., p. 22) that, when quindoline methiodide,



is treated with sodium hydroxide, it forms a  $\phi$ -base, *methylquindolanol*, which, it is now found, has the annexed formula; it crystallises from methyl alcohol in tiny needles. The application of the Zincke method showed that no methoxy-groups were present. A. McK.



**Preparation of Aromatic Monoacetyltriamines.** FARBER (FABRICAT. VOL. 1, FRIDR. BAYER & Co. (D.R. P. 183843)).—The aromatic monoacetyltriamines have hitherto not been obtained by the reduction of aromatic 2:4-dinitroacetylaminos owing to the resultant condensation between the contiguous amino and acylamino-groups leading to the production of the anhydrobases of the iminazole series. It has now been found that reduction without condensation can be effected by the use of mild reducing agents, such as iron and dilute acetic or mineral acids.

*N-Acetylmono- $\phi$ -phenylenetriamine*,  $NHAc \cdot C_6H_3(NH_2)_3$ , prismatic crystals, m. p. 158–159°, results from the mild reduction of 2:4-dinitroacetylaminide, when heated above its melting point or when boiled with glacial acetic acid, it loses water, forming aminomethylbenzimidazole.

*2,4-Acylamino-3,5-tolylethylenetriamine*,  $NHAc \cdot C_6H_3Me(NH_2)_3$ , yellow needles, m. p. 210–211°, is less soluble than the preceding base, and is obtained from 3:5-dinitroacetylaminide in a similar manner. Favourable results are obtained by substituting these new bases for the ordinary meta-diamines in the production of azo-dyes.

G. T. M.

[Preparation of Triaminotriphenylethylene.] GEORGES LAMBERT and CONSTANTIN FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R. P. 180011).—Trichloro- or tribromo-ethylene or acetylene tetrachloride, or the

**Oxazine Dyes.** RUDOLF NISTZKI and VICTOR BECKER (*Ber.*, 1907, 3397—3400).—1:4-Diamino-2-naphthol forms a stable hydrochloride,  $C_{10}H_8ON_2 \cdot 3HCl$ , which attacks the mucous membrane. The base rapidly turns brown on exposure to the air. A base obtained by, *disaminonaphthoxazon*,  $NH_2 \cdot C_{10}H_7 \cdot \langle \overset{N}{\underset{O}{\parallel}} \rangle \cdot C_{10}H_7 \cdot NH_2$ , is obtained when an alcoholic solution of this hydrochloride is boiled with crystals of sodium acetate while a current of air is passed through the solution. It forms well-developed, glistening crystals. A crystalline hydrochloride,  $C_{20}H_{16}ON_2Cl$ , is formed when the base is dissolved in phenol, precipitated with alcohol and hydrochloric acid, and dried at 60°. It dyes cotton mordanted with tannin, and its alkaline and acidic acid solutions exhibit a brilliant red fluorescence. When the almonosulphonic acid, known as eikonogen, is used in place of the laminonaphthol, a *disulphonic acid* derivative of the above dye is obtained.

1:4-Diamino- $\beta$ -naphthol 6-sulphonic acid yields a *disulphonic acid* derivative, which dyes wool in an acid bath in the blue.

**Synthesis of Iminoazolyethylamine [4- $\beta$ -Aminoethylglyoxaline].** ADOLF WINDAUS and W. VOGT (*Ber.*, 1907, 40, 1001).—The recognition that glyoxaline radicles are contained in the alkaloid pilocarpine (Jowett, *Trans.*, 1903, 83, 438) and in substances derived from proteins like histidine (Pauly, *Abstr.*, 1904, 1, 1065) has suggested the synthesis of these natural products. As a step in the reaction, glyoxaline-4-propionic acid (*Abstr.*, 1903, 1, 834) has been converted into 4- $\beta$ -aminoethylglyoxaline,  $\begin{matrix} NH \cdot CH_2 \\ | \\ CH=N \end{matrix} \cdot C \cdot CH_2 \cdot CH_2 \cdot NH_2$ , by means of Curtius' method.

*Ethyl glyoxalinepropionate* is a colourless oil, obtained by esterification and purification by means of the *oxalate*, which crystallises in rhombic plates, m. p. 158°; the *picrolonate* forms light yellow needles, m. p. 226° (decomp.). The *hydrazide*,  $C_8H_{10}ON_4$ , obtained by the reaction of the ester and 50% hydrazine hydrate, has m. p. 112°. The *hydrochloride* of aminoethylglyoxaline is obtained in 50% yield by treating an alcoholic solution of the hydrazide with amyl nitrite and hydrochloric acid to form the azoimide, decomposing this to obtain the urethane, and finally hydrolysing the urethane. It crystallises in needles, m. p. 240° (decomp.). No sparingly soluble salts are given by concentrated zinc or silver hydroxides in contradistinction to other glyoxaline compounds. The *platinichloride* is orange, blackens toward 100°, but does not melt; *picrate*, m. p. 239° (decomp.); *picromercurate* is black, m. p. 266° (decomp.). By treating the aminoethylglyoxaline with benzoyl chloride and

Ben. 170.  
NPh·CH<sub>3</sub>  
p. 117.

# Behaviour of Hydrogen Cyanide towards Phenylcarbamide

WALTER DICKMANN and HEINRICH KÄMMERER (*Ber.*, 1907, 37, 3743. Compare Abstr., 1905, i, 874).—By the action of sodium ethoxide, diphenylparabanimide is converted into the liquid

di-phenylguanidine,  $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$ , m. p. 225°, which

in colourless prisms, has acid properties, and is hydrolysed by

concentrated hydrochloric acid yielding aniline and phenylparabanic

acid, m. p. 209–210°. The two new compounds are also obtained by

condensation of ethyl oxalate with diphenylguanidine and phenyl

parabanamide respectively in the presence of sodium ethoxide.

Phenylparabanamide (oxalyldiphenylguanidine), m. p. 225°, which

is obtained most conveniently by warming diphenylguanidine with

glacial acetic acid, is also converted by sodium ethoxide into

di-phenylguanidine.

With phenylcarbamimide at 120°, diphenylparabanimide yields the

rhombic,  $\text{NPh}\cdot\text{CO}\cdot\text{N}\cdot\text{C}\begin{smallmatrix} \text{CO}\cdot\text{NPh} \\ \text{NPh}\cdot\text{CO} \end{smallmatrix}$ , m. p. 233°, which is the

final product of the action of hydrogen cyanide on phenyl

parabanamide (*loc. cit.*). By prolonged heating with glacial acetic acid, the

rhombic yields diphenylparabanic acid, whereas hydrolysis by

boiling of hydrochloric and glacial acetic acids forms in addition

phenylparabanamide.

Phenylparabanamide is hydrolysed by boiling acetic acid yielding

phenylparabanamide and small quantities of aniline and acetanilide; by

boiling with hydrochloric acid giving ammonium chloride, aniline hydro-

chloride, and carbon dioxide, and by boiling with water forming diphenyl

parabanamide, ammonia, aniline, and carbon dioxide. C. R.

## Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives. I and II. Cyanogen. ALEXANDER

BAITONER and E. AZZARELLO (*Atti R. Acad. Lincei*, 1907, [7], 16,

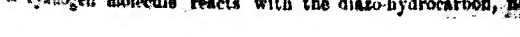
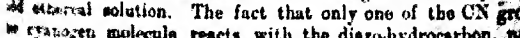
227–243, 318–328. Compare Azzarello, Abstr., 1905, i, 867).—

A ethereal solution of cyanogen reacts violently with a 2–5% ethereal

solution of diazomethane or diazoethane, forming a cyanogen

derivative of osotriazole, which, unless special precautions are taken,

undergoes etherification by the diazomethane:



In order to prevent the etherification, a very small amount of the

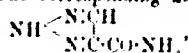
compound must be treated with a large excess of cyanogen in

an ethereal solution. The fact that only one of the CN groups in

the cyanogen molecule reacts with the diazo-hydrocarbon, no com-

being formed, would indicate a structure other than  $\text{NH} \begin{smallmatrix} \text{N} \text{CH} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CN} \end{smallmatrix}$  for cyanogen. The balance of evidence, which the authors review, is, however, in favour of the above formula.

**3-Cyano osotriazole**,  $\text{NH} \begin{smallmatrix} \text{N} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CN} \end{smallmatrix}$ , separates from benzene in small, white crystals, m. p. 113–114°, and gives precipitates with salts of many heavy metals. The corresponding amide,



prepared by the action of alcoholic potassium hydroxide on the cyanide compound, is deposited from alcohol in small, white crystals, m. p. 256–257°. When treated with 40% alcoholic potassium hydroxide solution, or with concentrated hydrochloric acid, it yields the osotriazole carboxylic acid described by Baltzer and von Pechmann (Ann., 1891, 1116), and this, when heated at 230–240°, is converted into the osotriazole prepared by these authors.

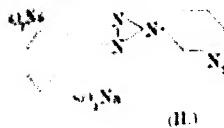
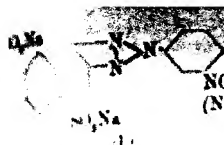
**3-Cyano-1-methylsotriazole**,  $\text{NMe} \begin{smallmatrix} \text{N} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CN} \end{smallmatrix}$ , is a colourless, neutral liquid, b. p. 95–30 mm., having a fruity odour. When treated with 40% alcoholic potassium hydroxide, it is converted into the potassium derivative of 1-methylsotriazole-3-carboxylic acid,  $\text{NMe} \begin{smallmatrix} \text{N} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CO}_2 \text{K} \end{smallmatrix}$ , which is deposited from acetone in minute, small, white crystals, m. p. 141–142°. The potassium, calcium, barium,  $(\text{C}_6\text{H}_5\text{O}_2\text{N}_3)_2\text{Ba} \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , and calcium salts, and the silver salt,  $\text{C}_6\text{H}_5\text{N}_3\text{HMeCO}_2\text{Ag}$ , b. p. 115–60 mm., were prepared.

**4-Cyano-3-methylsotriazole**,  $\text{NH} \begin{smallmatrix} \text{N} \text{CMe} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CN} \end{smallmatrix}$ , separates from benzene in small, white crystals, m. p. 84°, b. p. 160–30 mm., has the normal molecular weight in freezing acetic acid, and, in aqueous solution, has an acid reaction. The silver derivative,  $\text{C}_6\text{H}_5\text{N}_3\text{Ag}$ , is a white powder stable towards light.

**3-Methylsotriazole-4-carboxylic acid**,  $\text{NH} \begin{smallmatrix} \text{N} \text{CMe} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CO}_2 \text{H} \end{smallmatrix}$ , separates from water in shining, acicular crystals, m. p. 214–5°, and the calcium salt,  $(\text{C}_6\text{H}_5\text{O}_2\text{N}_3)_2\text{Ca}$ , was prepared.

**4-Cyano-3-methyl-1-ethylsotriazole**,  $\text{NEt} \begin{smallmatrix} \text{N} \text{CMe} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CN} \end{smallmatrix}$ , is a colourless liquid, b. p. 105–28 mm. **3-Methyl-1-ethylsotriazole-4-carboxylic acid**,  $\text{NEt} \begin{smallmatrix} \text{N} \text{CMe} \\ \diagup \quad \diagdown \\ \text{N} \text{C} \text{CO}_2 \text{H} \end{smallmatrix}$ , crystallises from benzene in shining, white needles, m. p. 131°; its calcium salt,  $(\text{C}_6\text{H}_5\text{N}_3\text{O}_2)_2\text{Ca}$ , was prepared. I. H. F.

[8-Aminophenyl]- $\alpha\beta$ -naphthatriazole-6:9-sulphonic Acid.] ARTEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 174545).—Sodium 3-nitrophenyl- $\alpha\beta$ -naphthatriazole-5:9-sulphonate.



(I) was prepared by coupling *m*-nitrodianiline chloride with  $\alpha$ -naphthylamine-3:8-disulphonate in sodium carbonate solution, and (NH<sub>4</sub>) then, after 20 hours, warming the liquid to 70–75° and adding aqueous sodium hypochlorite. The product was salted out and reduced with iron filings and water acidified with hydrochloric acid; the solution was rendered alkaline with sodium carbonate and 3-amino-phenyl- $\alpha\beta$ -naphthatriazole-4:9-disulphonic acid (I) precipitated from the filtrate by adding hydrochloric acid and sodium chloride. The azo-derivative (II), obtained by coupling the aminotriazole with  $\beta$ -naphthol-3:6-disulphonic acid, when dissolved in water and treated with a solution of barium chloride and a little aluminium hydroxide, yields a brilliant reddish-lake which is remarkably stable to light. G. T. M.

**The Mechanism of the Indamine and Azine Synthesis.** Willstätter's Paper on Aniline Black. HANS TH. BECHERER (*Ber.*, 1907, 40, 3412–3419. Compare this vol., i, 611).—The syntheses of indamines, azines, thiazines, and oxazines are represented by a single scheme, based on the two following facts. (1) The readiness with which *ortho*- and *p*-diamines, aminophenols, dihydroxy derivatives, and the corresponding sulphur compounds are oxidised. (2) The readiness with which monamines, diimines, quinols, and the corresponding sulphur compounds form additive compounds. In addition, attention is drawn to the readiness with which groups attached to nitrogen, nitrogen, or sulphur wander into the nucleus. The two reactions, which occur alternately in the case of a *p*-diamine, may be represented as (a) *p*-diamine + O → *p*-diimide and (b) *p*-diimide + HX → *p*-diamine with the X group attached to nitrogen. Several examples are worked out in detail, more especially the formation of safranine, methylene-blue, and Meldola's blue. Also the formation of 2:2-diaminoazobenzene from *o*-quinonediimine and of diaminodiphenyl from the oxidation product of benzidine. Willstätter's formula for aniline black is criticised. G. J. S.

**Action of Hydroxylamine on Safranones.** OTTO FISCHER and FRIEDRICH BERGER (*Ber.*, 1907, 40, 3406–3411. Compare Fischer and ARND, this vol., i, 94; Kehrman and Prager, *ibid.*, 447).—Kehrman and Prager's view of the constitution of the aminoisoresindone, obtained by the action of hydroxylamine on isoresindone, is confirmed, since the ethers obtained by the action of alkyl iodides and potassium hydroxide on the corresponding hydroxyisoresindone are not identical with the ethers of naphthasafranols. The *ortho*-position of the methoxy-

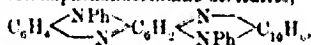
It appears that only those isosindones and amino-derivatives of phenylamine which are free from substituents in the two positions with respect to the quinone oxygen. Thus *o*-methoxyisorosindone, and *β*-*o*-methyliisorosindone (Abstr., 1904, 417) do not yield amino-derivatives.

Safranin does not yield an amino-derivative with hydroxylamine, but safranin ethyl ether yields *o*-aminosafranin ethyl ether,  $C_{27}H_{31}ON$ , which crystallises from alcohol in brilliant brown plates, m. p. 250°. The addition of concentrated hydrochloric acid to the alcohol or acetic acid solution produces a yellowish-green coloration. The corresponding methyl ether is less soluble in alcohol.

*o*-Anilinoisorosindone,  $C_{27}H_{31}ON$ , obtained by heating isosindone with aniline and aniline hydrochloride at 150° crystallises from alcohol in bronze coloured needles, m. p. 282—284°.

A naphthylfluorindine,  $C_{26}H_{24}N_2$ ,  $\langle \text{NH} \rangle \text{C}_6\text{H}_4 \langle \text{N} \rangle \text{C}_{10}\text{H}_7$ , is obtained when *o*-aminoisorosindone, *o*-phenylenediamine, and its hydrochloride are heated with ethyl alcohol at 140—150° for three hours. It crystallises from pyridine in golden-bronze, glistening plates, which dissolve in glacial acetic acid yielding a pure blue solution. The same product is formed when isorosindone is used instead of its amino-derivative, and even more readily from isorosinduline salts and *o*-phenylenediamine (compare Fischer and Hepp, Abstr., 1896, i, 323).

*o*-Aminoisorosindone, or isorosindone, when heated with *o*-aminodiphenylamine, its hydrochloride, and absolute alcohol at 150° for ten hours, yields a green naphthylfluorindine derivative,



which crystallises from dimethylaniline in prisms.

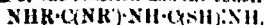
Aminoisorosindone, or isorosinduline, and *o*-naphthylendiamine also yield a green dye. These naphthylfluorindine dyes exhibit but feeble fluorescence except in concentrated sulphuric acid or pyridine solution (compare Nietzki and Vollenbruck, Abstr., 1904, i, 1662). J. J. S.

**Disulphides with Neighbouring Double Linkings. Action of Amines and Hydrazines on Thiourets. New Synthesis of Triazoles. II.** EMIL FROMM & EMIL VETTER (Ann., 1906, 366, 178—196. Compare Fromm, Abstr., 1906, i, 656; Fromm and Schneider, *ibid.*, 656, 714; Hantzsch and Wolvenkamp, *ibid.*, 1904, i, 919).—Perthiocyanic acid and thiouret undergo analogous reactions with potassium hydroxide, yielding sulphur and potassium cyanaminedithiocarbonate and phenyliminocyanaminedithiocarbonate respectively. The present work was undertaken to determine if thiouret reacts with aniline and phenylhydrazine in a manner analogous to the reaction of perthiocyanic acid with these reagents, which leads to the formation of phenyldithiobiuret and derivatives of triazole respectively.

When heated with aniline on the water-bath in absence of a solvent, phenylthiouret hydrochloride yields thiocarbamilide, but if the reaction

This crystallizes in white needles, m. p. 167°, forms a benzyl derivative,  $C_{16}H_{15}N_3S \cdot HCl$ , m. p. 179°, and on treatment with benzyl chloride and alcoholic sodium hydroxide yields the benzyl derivative,  $C_{16}H_{15}N_3S$ , m. p. 187°.

The constitution of the products of the action of amines on thiocarbonyl diisocyanides is confirmed by the formation of isomeric substances from *p*-phenylthiouret hydrochloride and *p*-phenetidine, on the one hand, and from *p*-phenethylthiouret hydrochloride and aniline, on the other hand. The products of the reaction had the constitution



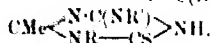
but two combinations would yield the same substance.

*p*-Phenylguanidophenylthiocarbamide,  $C_{16}H_{15}ON_3S$ , formed from phenylthiouret hydrochloride and *p*-phenetidine, crystallises in leaflets, m. p. 167°, and forms a benzyl derivative,  $C_{22}H_{21}ON_3S$ , m. p. 230°.

The action of *p*-phenetidine on perthiocyanic acid leads to the formation of *p*-phenethylthiobiuret,  $C_{16}H_{15}ON_3S$ , crystallising in leaflets, m. p. 178°, and di-*p*-phenethylthiocarbamide,  $C_{22}H_{21}O_2N_2S$ , crystallising in leaflets, m. p. 170°.

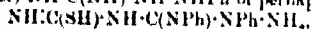
*p*-Phenethylthiouret hydrochloride,  $C_{16}H_{15}ON_3S \cdot HCl \cdot H_2O$ , m. p. 187°, reacts with aniline, forming phenylguanido-*p*-phenethylthiocarbamide, m. p. 179°. This yields a benzyl derivative,  $C_{22}H_{21}ON_3S$ , crystallising in leaflets, m. p. 166°.

The arylguanidoarylythiocarbamides form acetyl derivatives,  $OR \cdot C(S \cdot NH \cdot C(NR) \cdot NH) \cdot NHAc$ , which are converted by the action of thionyl chloride into anhydro compounds:  $CMc \cdot \begin{matrix} N \cdot C(NR) \\ | \\ S \cdot C(NR) \end{matrix} > NH$  or

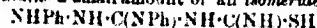


*Acetylbenzylguanidophenylthiocarbamide*, R and R' = Ph, m. p. 240°, is an anhydro compound, needles, m. p. 200°; when heated with benzyl chloride and potassium hydroxide, it forms the benzyl derivative of benzylguanidophenylthiocarbamide. *Acetyl-p*-phenethylguanidophenylthiocarbamide, m. p. 183°; the anhydro compound, m. p. 204°. *Acetylbenzylguanido-p*-phenethylthiocarbamide, needles, m. p. 172°; the anhydro compound, m. p. 187°.

When heated with phenylhydrazine in alcoholic solution, phenylthiouret hydrochloride forms sulphur and anilguanidophenylthiocarbamide,  $NPh \cdot C(SH) \cdot NH \cdot C(NH) \cdot NH \cdot NHPh$  or perhaps



which separates from alcohol in crystals, m. p. 167°, and if heated with alcoholic sodium hydroxide or dilute hydrochloric acid yields 3-amino-1-phenyl-1,2,4-triazole or its hydrochloride (Fromm and Göncz, *loc. cit.*, p. 572). The filtrate from the preparation of anilguanidophenylthiocarbamide contains a small amount of an isomeride,



or  $NH \cdot NPh \cdot C(NH) \cdot NH \cdot C(NPh) \cdot SH$ , which on successive treatment with sodium hydroxide and hydrochloric acid yields 5-amino-3-anilino-1-phenyl-1,2,4-triazole hydrochloride (Fromm and Göncz, *loc. cit.*).

*Anilguanido-p*-phenethylthiocarbamide,  $C_{16}H_{15}ON_3S$ , m. p. 168°



(decane), when boiled with excess of 95% alcohol solution yields 3-amino-5-*p*-phenylthio-1-phenyltriazole,  $C_{16}H_{11}ON_3$ , m. p. 137°; the hydrochloride of this,  $C_{16}H_{11}ON_3 \cdot HCl$ , crystalline in thin plates, m. p. 68°. The acetyl derivative,  $C_{18}H_{13}O_2N_3 \cdot H_2O$ , crystalline in needles, m. p. 145—148°.

Aminophenylguanido-*p*-phenylthiocarbamide,  $C_{16}H_{11}ON_3$ , obtained from the mother-liquor from the preparation of its isomer, crystallises in white leaflets, m. p. 236°; and when treated successively with sodium hydroxide and hydrochloric acid yields 3-amino-5-*p*-phenylthio-1-phenyltriazole hydrochloride, m. p. 175°, which is sparingly soluble. The free triazole forms a gelatinous mass and is readily soluble in alcohol.

**isoPurone.** JULIUS TAFEL and PERCY ALFRED HODGSON (*Ber.*, 1907, 40, 3743—3751. Compare Tafel, *Abstr.*, 1901, i, 215). The products obtained by the electrolytic reduction of uric acid are treated with concentrated ammonium hydroxide to separate the isouric acid, with sodium hydroxide to remove isopurone, and the residue yields purone by crystallisation from hot water. *isoPurone* is a saturated substance which can be estimated by iodine and thionine. The molecular weights of purone and of isopurone determined in aqueous solution by the ebullioscopic method correspond with the formula  $C_4H_4O_2N_2$ .

*isoTetrahydropuric acid*,  $C_4H_4O_2N_2$ , prepared by the action of purone on an aqueous solution of isopurone at 0°, crystallises in slender needles, decomposes at 200°, has a neutral reaction, and decomposes readily in alkalis. A boiling solution of barium hydroxide converts it into the yellow barium salt of  $\alpha$ -isouracil,  $C_4H_2O_2N_2$ , from which careful treatment with 2*N* hydrochloric acid at 21° liberates  $\alpha$ -isouracil,  $C_4H_4O_2N_2$ . This substance crystallises in needles, decomposes at 350°, has an acid reaction, dissolves in dilute alkali, decolorises bromine water, and gives a violet brown coloration with ferric chloride.

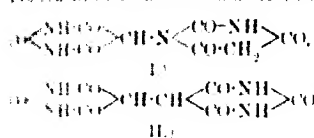
The mother-liquor from which the barium salt of  $\alpha$ -isouracil has been precipitated contains  $\beta$ -isouracil,  $C_4H_4O_2N_2$ , which crystallises in slender needles, has a neutral reaction, dissolves in dilute alkali, and forms a crystalline substance with phenylhydrazine which seems to be a hydrazone.

**Reduction of Theophylline and Paraxanthine.** JULIUS TAFEL and JULIUS DOHR (*Ber.*, 1907, 40, 3752—3757. Compare *Abstr.*, 1900, i, 121). The electrolytic reduction of theophylline in 5*N* phosphoric acid at the ordinary temperature, with prepared lead anode and a current density of 12 amperes per sq. dem., results in the formation of *deoxytheophylline*,  $C_7H_{10}ON_4$ , which separates from hot water in crystals containing 3H<sub>2</sub>O, darkens at 200°, and has m. p. 215—225°, has a faintly alkaline reaction, and is soluble in dilute acids or alkalis; the hydrochloride and the picrate are prepared. By the action of bromine in cold glacial acetic acid, the substance yields *bromodeoxytheophylline*,  $C_7H_9ON_4Br$ , which is converted by sodium hydroxide into *oxydeoxytheophylline*,  $C_7H_{10}O_2N_4 \cdot 2H_2O$ .

Analogue compounds are obtained from paraxanthine by similar treatment. *Deoxyparaxanthine*,  $C_7H_7ON_3$ , crystallises from water with 11 H<sub>2</sub>O, decomposes at 250°, has a neutral reaction, and is not more soluble in dilute alkalis than in water. *Bromodeoxyparaxanthine*,  $C_7H_6ON_3Br$ , dissolves in water to a strongly acid solution, and is converted by sodium hydroxide into 6-hydroxydeoxyparaxanthine,  $C_7H_8N_3O_2$ , which darkens at 230°. C. S.

**Acidity of Deoxyxanthines.** JULIUS TAFEL and JULIUS DOER (Ber. 1907, 40, 3757–3759. Compare preceding abstract). It has been shown that deoxyxanthine, 3-methyldoxyxanthine, and deoxytheoxanthine, unlike deoxyheteroxanthine, deoxyparaxanthine, and deoxyisoxanthine, are more soluble in dilute alkalis than in water. The authors have measured the strengths of these compounds by the method (Trans., 1906, 89, 1839) and arrive at the conclusion that the deoxyxanthines are weaker acids than the xanthines, and that in the deoxyxanthines the acid properties are conferred solely by the pyrimidine ring. C. S.

**Hydurilic Acid.** MAX CONRAD (Annalen, 1907, 356, 24–31).—Two constitution isomers have been ascribed to hydrilic acid (I and II).

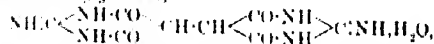


The author shows that the constitution II is the correct one. Since barbituric acid when heated with concentrated hydrochloric acid is hydrolysed forming carbon dioxide, ammonia, and acetic

acid, and if of the constitution II must under the same conditions yield acetic acid, ammonia, and succinic acid. It is found that when heated with concentrated hydrochloric acid at 200–230°, hydrilic acid yields succinic acid in almost quantitative amount.

The constitution II is supported also by the formation of hydrilic acid by condensation of ethyl ethanetetra-carboxylate with carbamide by means of alcoholic sodium ethoxide at 60–70°, and together with small amounts of succinic acid by hydrolysis of ethanetetra-carbonyl-urea by means of dilute hydrochloric acid at 150°.

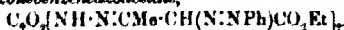
*Ethanetetra-carbonylguanide*,



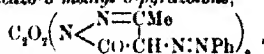
is prepared in a 62% yield by heating ethyl ethanetetra-carboxylate with guanidine hydrochloride and sodium ethoxide in alcoholic solution at 50°. It crystallises in needles, decomp. when heated, is readily soluble in alkali hydroxides or carbonates, separates in prisms on prolonged heating of its ammoniacal solution, and dissolves in cold nitric acid. The silver salt,  $C_6H_4N_4Ag_2 \cdot 2H_2O$ , was analysed; the hydrochloride crystallises in white needles. Ammonium hydrilic acid gives a green coloration with ferric chloride, becoming colourless on addition of hydrochloric acid or on heating, and forms a red solution with potassium bismate in acetic acid. G. Y.

...and Oxalohydrazone. Compare *Ann.* (and, in part, *Ber.*) **LXXXI** (1907, 40, 3787—3798).—The two methylene groups in ethyl oxalylbis-hydrazonoacetate (Bülow and Lobeck, this vol., i, 301) are capable of reacting, like the methylene group in compounds of the type  $\text{COR}\cdot\text{NH}\cdot\text{N}\cdot\text{CR}'\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$ , with diazobenzene chloride to form the formation of *o*-azobenzylhydrazones. These azo-derivatives, generally speaking, far more stable than the parent substances.

*Ethyl oxalylbis-hydrazono-benzeneazobenzeneacetate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{N}\cdot\text{NPh})\cdot\text{CMo}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMo}\cdot\text{CH}(\text{CO}_2\text{Et})$ , obtained by the action of diazobenzene chloride on ethyl oxalylbis-hydrazonoacetate in alcoholic solution in the presence of sodium acetate at low temperatures, crystallises in yellow, felted needles, m.p. 155° (unsharp); at the same time, is formed a small quantity of *oxalylbis-hydrazono-benzeneazobenzeneacetate*,



The latter compound alone is produced by using very dilute solutions, but is better prepared by the interaction of oxalylhydrazonoacetate and benzeneazobenzeneacetate in alcoholic or acetic acid solution. It forms colourless crystals, swells and froths up at 211—212° and 211—212° and decomposes slightly above this temperature into *o*-azobenzyl and 1:1-oxalylbis 4-benzeneazo-3-methyl-5-pyrazolone,



obtained as a yellowish-red, crystalline powder, m. p. 256—257°. The compound is decomposed by hot potassium hydroxide solution or pyridine into oxalic acid and 4-benzeneazo-3-methylpyrazolone (compare von Rothenburg, *Abstr.*, 1895, i, 686).

Ethyl oxalylbis-hydrazono-benzeneazobenzeneacetate is decomposed on boiling with phenylhydrazine in acetic acid solution with the formation of alcohol, oxalylhydrazide, and 4-benzeneazo-1-phenyl-5-methylpyrazolone.

The author replies to the criticisms of Curtius, *Ber.*, 1895, **LXX** (this vol., i, 451). W. H. Q.

**Action of Diazobenzene Chloride on *p*-Hydroxybenzoic Acid.** EUGEN GRANDMOUGIN and H. FREIMANN (*Ber.*, 1905, **LXXXVI**, 3433—3454. Compare Limpricht, *Abstr.*, 1891, 1036).—Diazobenzene chloride reacts with a solution of *p*-hydroxybenzoic acid in the presence of sodium carbonate, yielding bis-benzeneazophenol and a small amount of benzeneazo-*p*-hydroxybenzoic acid (Abstr., 1897, i, 341). In the presence of sodium hydroxide, the chief product is tris-benzeneazophenol (this vol., i, 165).

**Preparation of 1-Diazo- $\beta$ -naphtholdi- and trisulphonic Acids.** KALLE & Co. (D.R.-P. 184477).—The 1-amino- $\beta$ -naphthol monosulphonic acids are diazotised normally with sodium nitrite in the presence of organic acids (*Abstr.*, 1905, i, 161); the corresponding di- and tri-sulphonic acids are readily converted into diazo-derivatives in the presence of sulphuric acid, provided that dilute solutions of

coloured at first, but from the yellow solution, it has been

**The Diazotisation of 1-Amino- $\beta$ -naphtholsulphonic Acids.** **MELLENHART** *VER. CHEMISCHE INDUSTRIE IN BASEL* (D. 11714).—The interaction of nitrous acid and the 1-amino- $\beta$ -naphtholsulphonic acids leads to the production of quinonoid substances, but the reaction is largely one of oxidation. If, however, the acids of these 1-amino- $\beta$ -naphtholsulphonic acids are acetylated (the amino group with acetic anhydride, then the acetyl derivative is obtained furnish yellow, crystalline diazo-compounds, such as acetyl-1-diazonaphthalene-4-sulphonic acid, which, on treatment with dilute aqueous alkalis, lose their acetyl group and give rise to the corresponding 2-hydroxy-1-diazonaphthalenesulphonic acids. This elimination of acetyl may be effected similarly after combining the acetyl-1-diazonaphthalenesulphonic acid with phenol and aromatic amines, and in this way 2-hydroxyazonaphthalene colouring matters are produced which may be employed as mordant dyes. G. T. M.

**Diazo-derivatives of Salicylic Acid.** **EGGEN GRANDMOUGIN**, E. GORDAN, and H. FREIMANN (*Ber.*, 1907, 40, 3450—3453. Compare Langricht, *Abstr.*, 1891, 1036).—A mixture of bisbenzenesalicylic acid, benzenesalicylic acid, and the triazo-derivative of benzol (this vol., i, 664) is formed when a solution of diazobenzene chloride and salicylic acid dissolved in sodium hydroxide is kept at 0° for some five days. The monoazo-compound remains dissolved in the alkaline solution, and may be precipitated by the addition of acid. The *benzenesalicylic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_4(\text{N}_2\text{Ph}) \cdot \text{CO}_2\text{H}$ , may be extracted with hot dilute sodium hydroxide solution, and crystallises from chloroform in reddish brown, felted needles, m. p. 218°. With sulphuric acid, it gives the colorations characteristic of bisazo-compounds, and when reduced with stannous chloride yields 3:5-diaminosalicylic acid.

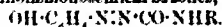
The acetyl derivative of the bisazo compound has m. p. 196°. *Bis-benzenesalicylic acid*,  $\text{C}_{22}\text{H}_{18}\text{O}_5\text{N}_4$ , forms dark violet crystals with metallic lustre, m. p. 170°, and yields an acetyl derivative, m. p. 173°. *o-Toluenesalicylic acid*,  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$ , forms yellowish-brown needles, m. p. 191°, and yields an acetyl derivative, m. p. 145°.

*Tri- $\alpha$ -toluenesulphophenol*,  $\text{C}_9\text{H}_7\text{ON}_3$ , forms bronze-coloured needles, m. p. 128°, and its acetyl derivative orange-coloured needles, m. p. 135°. Diazotised nitroanilines yield monoazo-derivatives together with bisazo-derivatives of phenol.

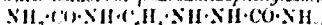
*Bis- $p$ -nitrobenzenesulphophenol*,  $\text{C}_{18}\text{H}_{12}\text{O}_6\text{N}_6$ , crystallises from nitrobenzene or tetrachloroethane in brown, felted needles, and its acetyl derivative has m. p. 208°. J. J. S.

**Aromatic-aliphatic- $p$ -aminoazo-compounds.** **WALTER BARNER** and A. REICHAUER (*Ber.*, 1907, 40, 3806—3815).—The

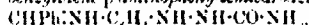
oxidation products of quinoneoxime and semicarbazone (Borache, Abstr., 1906, i, 319) are converted on reduction with tin and hydrochloric acid and subsequent oxidation, into aromatic azo-compounds of the type  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , depending with the quinonemonosemicarbazones,



The reduction of either *p*-nitrophenylsemicarbazide (H. J. Abstr., 1899, i, 638) or benzquinone oximesemicarbazone (Thiele, Abstr., 1899, i, 47) with tin and hydrochloric acid results in the formation of *p*-aminophenylsemicarbazide (*p*-amido benzoylformamide) hydrochloride, colourless leaflets, decomposing at  $150^\circ$ ; ammonia liberates the free base,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , small, colourless needles, which rapidly oxidise in the air. A solution of the hydrochloride on treatment with potassium cyanate and ammonia yields deposits pearly, white leaflets of *p*-carbamidophenylsemicarbazide,



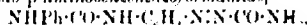
m. p.  $201-202^\circ$  (decomp.). Benzaldehyde reacts with the base in the formation of benzylidene-*p*-aminophenylsemicarbazide,



yellowish-white leaflets, m. p.  $204^\circ$  (decomp.).

*p*-Aminobenzeneazofornamide, obtained only in the form of hydrate,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$ , is prepared by the oxidation of the hydrazo-compound; it crystallises in dark red needles with a low reflex, m. p.  $125-126^\circ$  (decomp.). The molecule of water is removed by keeping the compound some days in a vacuum desiccator. It is converted by strong hydrochloric acid into a golden-brown hydrochloride, and is decomposed on heating with potassium hydroxide solution according to the equation:  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2 + 2\text{KOH} \rightarrow \text{NH}_2\text{Ph} + \text{N}_2 + \text{NH}_3 + \text{K}_2\text{CO}_3$ ; at the same time, a small quantity of benzidine is formed, which crystallises in brown needles. *p*-Carbamidobenzeneazofornamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$ , prepared by the action on a solution of the hydrazo-compound with ammonia and hydrogen peroxide, crystallises in small, brick-red needles, m. p.  $178^\circ$  (decomp.).

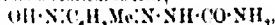
Phenylcarbamido-*p*-aminobenzeneazofornamide,



which results from the interaction of phenylcarbimide and the azo compound, crystallises in yellowish red needles, decomposing at  $172^\circ$ .

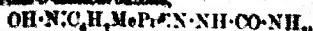
Benzoyl-*p*-aminobenzeneazofornamide,  $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , forms small, orange needles, m. p.  $218^\circ$  (decomp.). Benzene azo is the parent azo compound yielding 3:5(1)-dibromo-4-aminobenzeneazofornamide,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Br}_2\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2$ , small, yellow needles, m. p.  $183^\circ$ .

2-Toluquinoneoxime 5 semicarbazone,



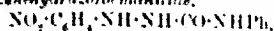
prepared by the interaction of 2-toluquinoneoxime and semicarbazide hydrochloride, is a brown, crystalline powder, decomposing at  $120^\circ$ . It yields, on reduction with tin and hydrochloric acid and subsequent oxidation of the hydrazo compound, 2-aminotoluene 5 semicarbazide,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$ , small, reddish-brown needles, m. p.  $85-86^\circ$  (decomp.). In the same way, are obtained 2-toluyloxy-

...small, brown needles, decomposing at 243°, and  
...5-aminobenzene-5-semicarbazone,



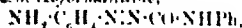
...small, yellow needles, m. p. 221–222°, which also give rise to amino-  
...compounds.

Phenylcarbamide combines with the three nitrophenylhydrazones,  
...nitrobenzenecarbazone, benzoyl derivative,

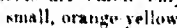


...small, slender, yellow needles, m. p. 220°, m-nitrobenzenecarbazone,  
...benzene, yellow leaflets, m. p. 220°, and p-nitrobenzenecarbazone,

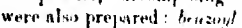
...small, yellowish-white needles, m. p. 220°. Both the latter  
...and benzoquinoneoximephenylsemicarbazone (Borsche and  
Klar, *Chem.*, 1906, i, 320) yield on reduction with tin and hydrochloric  
acid *p-nitrobenzenecarbazone*, small, colourless,  
...needles, which decompose and turn violet above 190°; sodium  
acetate liberates the free base,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , long,  
...needles, m. p. 187° (decomp.), which is converted on oxidation  
into *p-aminobenzenecarbazone*, benzoyl derivative,



...orange-red leaflets, m. p. 160–161° (decomp.). The salts of the  
...compound with acids are stable only in the presence of the  
...hydrochloride, small, orange-yellow needles; oxalate,



...dark brown, crystalline powder, decomposing at 186–187°. The  
...compounds were also prepared: benzoyl derivative,



...small, yellow needles, m. p. 219–220°, phenylcarbamide derivative,  
... $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CO}\cdot\text{NHPh}$ , reddish-yellow needles, decom-

posing at 210°, dibromo-derivative,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{N}_2\cdot\text{CO}\cdot\text{NHPh}$ , small,  
...yellow needles, m. p. 155–156°.

By the same methods as described above are obtained: 2-amino-  
...benzenecarbazone,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NHPh}$ , reddish-brown,  
...crystals, decomposing at 150–151°, and 3-aminotoluene-6-  
...carbazone, dark red needles with green reflex, m. p. 137°.

W. H. G.

**Action of Dilute Sulphuric Acid on Proteins.** LEO LANGSTEIN  
*Biochem. Zeitsch.*, 1907, 5, 410–412. Recent authors have stated  
that digestion of protein with 0.5% hydrochloric acid leads to the  
formation of the same end products as are found in gastric digestion,  
...more slowly. The present experiments confirm earlier views of  
...that protein is very resistant to dilute sulphuric acid.  
After eight months digestion in 1% acid at 37°, only 18% of dried  
...goes into solution; rather more of the other proteins  
...were dissolved. The dissolved  
...substances were completely precipitable by phospho-  
...acid.

W. D. H.

**Influence of Solutions of Pigments on the Heat Coagu-  
...ation of Proteins.** HANS ARON (*Biochem. Zeitsch.*, 1907, 5,  
413–415). Acid pigments (eosin and aurantia) or their free acids,

...ability of the system. The explanation suggested is that when a colloid is formed, in which the pigment acts towards the water as a "protective colloid."

**Dissociation of Serum-Globulin at Varying Hydrogen Ion Concentrations.** T. BRAILSFORD ROBERTSON (*J. Phys. Chem.*, 1907, 11, 437—460. Compare Abstr., 1906, ii, 828; *Harvey*, 1906, i, 121).—Equations are deduced by means of which a substance containing the ratio of the acid and basic constants,  $k_a$  and  $k_b$ , of an amphoteric electrolyte as serum-globulin can be calculated from two experimental observations. The hydrogen ion concentrations of globulin solutions containing varying proportions of acid were determined by means of concentration cells and the conductivities of globulin solutions to which varying proportions of acid had been added were also measured; from these data, by an indirect method, the value  $68.3 \times 10^{-4}$  was obtained for the expression  $Kk_a/k_b$ , where  $K$  is the dissociation constant for water. By another and probably more accurate method, the value  $265 \times 10^{-4}$  was obtained for the same expression. For the velocity of the serum-globulin in the water,  $1 \times 10^{-5}$  cm./sec. under a potential gradient of 1 volt/cm. was deduced, whilst Hardy (*loc. cit.*) by a direct method obtained  $10 \times 10^{-5}$  cm./sec.

Serum-globulin is a fairly strong acid, but its basic properties are slight that it behaves to alkalis as a non-amphoteric acid.

Some evidence has been obtained that solutions of proteins as more or less complex polymerides of the type  $HXOH$ , and that the equilibrium is displaced by the addition of acids, salts, &c. In the case of serum-globulin, therefore, there is no definite molecular concentration in acid solution, but in alkaline solution, owing to its slightly basic character, the degree of polymerisation and therefore the molecular weight is constant. The molecular weight of serum-globulin in alkaline solution is given as 1967, and the average molecular weight in acid solution as 1684, but the latter value is very uncertain.

**Formation of Polypeptides by the Hydrolysis of Proteins.** EMIL FISCHER and EMIL ANDERHILDEN (*Ber.*, 1907, 40, 2341—2349). In part already published (this vol., i, 737. Compare also 1906, ii, 718).—When treated with 70% sulphuric acid at 36–38°C. in presence of *Leucyl D* glutamic acid,  $[a]_D^{20} + 10.2$ , m. p. 232 (near identical with the synthetical product). Levene's claim to have first obtained a dipeptide from the decomposition products of proteins is not to be taken as accurate.

**Hydrolysis of Glycinin, the Globulin of the Soy Bean, and of the Crystalline Globulin of the Squash Seed (*Cucurbit maxima*).** THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Am. J. Physiol.*, 1907, 19, 468—474, 475—481).—Acid hydrolysis led to the following percentage results calculated on a moisture and ash-free basis for the two proteins mentioned:

protein .....	0.97	0.67	Serine .....	not isolated	not isolated
casein .....	not isolated	1.93	Tyrosine .....	1.86	1.93
albumin .....	0.68	0.36	Arginine .....	5.13	14.44
globulin .....	3.78	2.82	Histidine .....	1.39	3.40
myofibrin .....	3.86	3.32	Lysine .....	2.71	1.93
peptone .....	3.89	3.30	Ammonia .....	2.56	1.93
lactic acid .....	19.46	12.35	Tryptophan .....	present	present
acetic acid .....	8.45	7.32	Cystine .....	—	0.25

W. D. H.

**The Formation of Acetone from Acetoacetates by means of Organ-extracts and Proteins.** LEO POLLAK (*Beitr. chem. Physik*, 1907, 10, 232—250).—By digestion of sodium acetoacetate with sodium or organ-extracts, there is a rapid decomposition of the salt with the formation of carbon dioxide and acetone. The agent in the serum responsible for this is protein. Serum-globulin, and the serum albumin, caseinogen, Witte's peptone, amino-acids (serine, alanine, &c.) all have the same action. All these substances contain the amino-group.

W. D. H.

**Combining Power of Casein with Certain Acids.** JOHN H. JOHNSON (*Amer. Chem. Soc.*, 1907, 29, 1334—1342).—In previous papers (*Amer.*, 1905, i, 498; 1906, i, 391), it has been shown that casein combines with alkalis to form salts. It has now been found that casein combines with acids, and the behaviour of various acids has been investigated. At the ordinary temperature, 1 gram of dry casein unites with nearly 7 c.c. of N/10 hydrochloric, hydrobromic, and sulphuric acids, and acetic acid. It also combines with tartaric, ascorbic, and oxalic acids, but not with boric acid. If the casein solution is evaporated in presence of dilute acid, a large amount of the latter, in the case of hydrochloric acid, four times as much, enters into combination. This is due, to some extent at least, to the partial hydrolysis of the casein and the union of the acid with the products of such hydrolysis.

E. G.

**Action of Dilute Acids on Casein when Soluble Compounds are not Formed.** LUCIUS L. VAN SLYKE and DONALD D. VAN SLYKE (*Amer. Chem. J.*, 1907, 38, 383—456).—In a previous paper (*Abstr.*, 1907, i, 192) it has been shown that casein unites with acids to form soluble products. A study has now been made of the behaviour of casein with hydrochloric, sulphuric, lactic, and acetic acids of concentrations from N/125 to N/2000, at temperatures of 0°, 25°, and 45°, and during periods varying from five minutes to forty-eight hours. The results indicate that the insoluble substances formed are not salts, but are produced by adsorption of the acid by the casein. The precipitate produced when milk turns sour is casein containing adsorbed lactic acid. In carrying out the investigation, casein was shaken with dilute



acids of known strength, and, after filtration, the quantity of acid removed from the solution was calculated from the decrease in conductivity. Experiments were made to ascertain the concentration at which casein is soluble in dilute acids in order that such conditions might be avoided. It was found that the protein does not dissolve to an appreciable extent when left for several hours at 0 in acids of concentration of  $N/1000$  or less, but that the rate of solution increases with the concentration, the temperature, and the duration of contact. The rate at which casein dissolves in different acids of equivalent strength is not proportional to the concentration of the hydrogen ions or to the degree of dissociation, but is proportionately great for the weak organic acids. From dilute acids of equal concentration, the dissolved protein takes up a larger proportion of acid than the undissolved. The solubility of casein in dilute acids is probably due to decomposition of the protein. Casein neither dissolves in  $N/125$  magnesium sulphate or  $N/100$  calcium chloride nor adsorbs either of these salts.

The amount of acid withdrawn by casein from dilute solutions in which it does not dissolve varies with the concentration of the acid, the duration of contact until equilibrium is reached, the temperature of agitation until equilibrium is reached, the temperature, and the particular acid employed. The acid is never entirely removed from the solution.

Determinations have been made of the amount of each of these acids adsorbed by 1 gram of casein at the equilibrium point and the conditions at which equilibrium is produced under different conditions. The acid can be removed from the casein by shaking it with water.

**Sulphohæmoglobin.** T. WOOD CLARKE and W. H. HARRIS (*J. Physiol.*, 1907, **38**, 62-67).—Sulphohæmoglobin is regarded as a definite compound in aqueous solution. It could not be obtained in crystalline form. The action of carbon monoxide on hæmoglobin, or of hydrogen sulphide on carboxyhæmoglobin, produces a new compound, carboxysulphohæmoglobin. Reduction of oxyhæmoglobin is a necessary preliminary for the formation of sulphohæmoglobin. Selenohæmoglobin closely resembles sulphohæmoglobin.

W. P. H.

**Hair Pigment, Choroid Pigment, and other Melanins.** EDUARD SPIEGLER (*Beitr. chem. Physiol. Path.*, 1907, **10**, 236-261).—The pigment of melanotic livers is different from that of the hair, as both resemble the choroid pigment (from pigs' eyes) in that it contains hæmopyrrole, and so their origin from the blood is impossible. On decomposition of the pigments, acetone derivatives or acetone products of acetone residues are found; the differences between the products in the various pigments accounts for the differences of the pigments. The parent substances of the pigments are tyrosine and acetone; possibly other aromatic groups of the protein molecule such as phenylalanine and tyrosine, participate in their formation.

W. P. H.

**The Chemical Nature of the Fundamental Colouring Matter of Urine.** S. DONNOSKI (*Compt. rend.*, 1907, 145, 575-577).—The primary colouring matter, urochrome, has been prepared and named. It may be separated from fresh urine which has been freed from most of its salts by the addition of cupric acetate in a cold dilute alcohol medium. The analytical data are: C, 43.09; H, 5.14; N, 11.10; S, 5.09; O, 35.53. The free acid and its calcium and barium salts are soluble in water. It is readily decomposed by alkalis and by ferric salts or iodic acid. The acid contains a pyrrole group which reacts with diazo salts in much the same manner as pyrazole, but quite differently from hemipyrrole.

The pyrrole group, when exposed to the air, in an acidified alcoholic solution polymerises, and the product gives an absorption band identical with that observed in the spectrum of polymerised pyrrole. When heated with hydrochloric acid, urochrome is decomposed, yielding a black product: C, 59.16; H, 4.91; N, 9.69; S, 3.55; O, 22.69.

The normal amount of urochrome eliminated by the human organism in twenty-four hours varies between 0.4 and 0.7 gram, but in cases of febrile diseases, such as typhoid fever, increases considerably.

J. J. S.

**Nucleic Acid from the Pancreas (Guanylic Acid).** OTTO VON KERN and ERNST JERUSALEM (*Beitr. chem. Physiol. Path.*, 1907, 10, 1-16).—Bang states that guanylic acid, the nucleic acid obtained from the pancreas, differs from other nucleic acids, inasmuch as it yields a derivative of glycerophosphoric acid, yields one third of its weight on hydrolysis in the form of a reducing sugar, and contains only one basic substance, guanine. All these assertions are now alleged to be incorrect, and there is no necessity to distinguish between nucleic and other nucleic acids of animal origin.

W. D. H.

**Gelatin Forms Produced by Precipitates of Salts and Crystals.** RICHARD E. LIESEGANG (*Chem. Zentr.*, 1907, ii, 415; from *Monatsh. Chem. Ind. Kolloide*, 1, 364-367). Compare this vol., ii, 11. The formation of a precipitate, or of crystals of salt or water, by which gelatin to take certain forms or shapes which are retained after the cause has been removed. Experiments on the crystallisation of potassium chromate have shown that, contrary to Molisch's theory (*über das Erfrieren der Pflanzen*, Jena, 1897), the gelatin remains at the places where the crystals form. Experiments on water-gelatin films which had been dyed with methylene-blue showed, however, that both accumulation and dispersion of the gelatin is caused by the formation of crystals even in the same preparation.

E. W. W.

**The Amounts of Cystin in Various Horny Materials.** JOSEF BARTULA (*Zeitsch. physiol. Chem.*, 1907, 52, 474-481, compare *Münch. Abstr.*, 1900, i, 128; 1902, i, 331).—The following percentages of cystine have been obtained from the materials mentioned: human hair, 13-14.5; human nails, 5-15; horse hair, 7-9; ram's hoofs, 3-20; ox hair, 7-27; hoofs of oxen, 5-37; pigs' bristles, 12; pigs' hoofs, 2-17.

J. J. S.

**Nitrocellulose.** *Zeitsch. Naturh. Genuussn.*, 1907, 14, 256. (Abstr., 1906, i, 778).—The authors have found by warming nitric acid alone, or in the presence of sulphuric acid, or a mixture of nitrates corresponding in properties with the celluloses. The chitin dissolves in the acid, and the nitro-cellulose is precipitated by pouring the solution into water. Two products are formed, one of which is insoluble in all the ordinary organic solvents, whereas the other dissolves readily in alcohol, acetone, ether, and glacial acetic acid. They are true nitrates, as when treated with acids or alkalis they yield nitric acid.

Chitosan reacts with nitrous acid, yielding a product with properties soluble in water, acids, and alkalis, but precipitated by alcohol.

**Diamino-acids from Koilin.** ERICH VON KNAFFL (Z. physiol. Chem., 1907, 52, 472-473).—The following diamino-acids have been obtained by hydrolysing koilin (compare this with sulphuric acid: histidine 0.034, arginine 3.596, lysine 1.014). The numbers are parts per 100 of air-dried and ash-free koilin.

**A New Solvent for Some Proteins.** IWAN OSTER (J. pr. Chem., 1907, [ii], 76, 267-268).—As Fischer has shown the proteins are complicated amides, it was to be expected that they would prove to be soluble in simple amides. He found that the albumoses and peptones dissolve in formamide and acetamide. The latter dissolves over 30% of the peptone of egg albumin, whereas the albumins, such as egg- and serum albumins, do not dissolve in this solvent. The concentrated solution of albumins are viscid at the ordinary temperature, gradually become turbid, brown, and can be filtered. The solubility in formamide is useful in the separation of proteins from each other and from inorganic material. The solutions in acetamide are suitable for many analytical investigations.

**Hydrolysis of the Albumoses Occurring in Meat Extract.** KARL MICKO (*Zeitsch. Naturh. Genuussn.*, 1907, 14, 256).—The experiments described were undertaken for the purpose of ascertaining the origin of the amino-acids obtained in the hydrolysis of meat extract (Abstr., 1906, i, 778). The portion of meat extract precipitated by zinc or ammonium sulphate is not identical with either gelatin or gelatins, and unaltered gelatin cannot be detected in the extract itself. During the manufacture of meat extract gelatin does not pass into solution, but it is converted by the lactic acid present into gelatins or acid glutin. The greater part of the portion precipitated by ammonium sulphate consists of a mixture of proteins having the general properties of albumoses and showing no indication of having been derived from gelatin. A small proportion of the albumoses, however, gives reactions very similar to those obtained with gelatin, etc. Hydrolysis of the constituents of meat extract which are soluble in saturated ammonium sulphate solution yields monomino-acids.

**Congulones.** D. LAWSON (*Zeitsch. physikal. Chem.*, 1907, 53, 1-7). In the peptic digestion of proteins, as well as in their digestion by mineral acids, at least two types of conglutone-yielding substances are recognizable. The first are of the type of proteoses, and the substances which arise from them yield on hydrolysis monoamino acids and basic nitrogenous cleavage products. The second type of conglutone-yielding substances are of the type of polypeptides, and the substances which arise from them yield on hydrolysis only monoamino acids.

W. D. H.

**Racemic Tryptophan.** RUDOLF A. ALLERS (*Biochem. Zeitsch.*, 1907, 272-275).—Racemic tryptophan, prepared according to Ellinger's method, and the synthetic preparation of Ellinger and Neberg (this vol., i, 737) both begin to melt at 256°. Optically active tryptophan is stated to melt at 273° by Hopkins and Cole and Neberg and Popowsky; at 289° by Abderhalden and Kempe. Racemization is probably due to the ammonia added at 60° in the course of preparation (compare following abstract). G. B.

**Tryptophan.** CARL NEUBERG (*Biochem. Zeitsch.*, 1907, 3, 276-283). An aqueous solution, when added to tryptophan dissolved in alkali solution, produces a pale brown, amorphous precipitate having the spectrum of a mixture of mono- and di-iodotryptophan (compare Neberg and Popowsky, this vol., i, 253; Nurnberg, this vol., 283).

Silver nitrate added to tryptophan dissolved in slightly less than molar sodium hydroxide produces a silver salt,  $C_{11}H_{11}O_2N_2Ag$ . Tryptophan is racemized by concentrated hydrochloric acid at 170°, and melts at 254-255°. An optically inactive specimen was obtained by Neberg's method of preparation, which involves heating with lead carbonate and ammonia (compare preceding abstract). G. B.

**The Non-existence of Protagon as a Definite Chemical Compound.** OTTO ROSENHEIM and M. CHRISTINE TRUB (*J. Physiol.*, 1907, 30, 1-16).—Liebreich's, Gangee and Blankenhorn's, and other protagons represent the same substance as cerebrotose prepared Gmelin in 1834. A similar substance is obtained by extracting with boiling acetone after the cholesterol has been removed by diazotization. All these substances may be split into substances of varying phosphorus and nitrogen percentage by simple fractional crystallization at different temperatures, or with different reagents. They also show great difference in optical activity and in amount of galactose split off by acid hydrolysis. The base substance as well as choline is found amongst the products of acid hydrolysis. Protagon is not a definite chemical compound, but a mixture of substances, some of which (such as phrenosin) are nitrogen-free and others (such as sphingomyelin) rich in phosphorus.

W. D. H.

**Protagon.** WILLIAM J. GIES (*J. Biol. Chem.*, 1907, 3, 339-358). The non-identity of protagon as a chemical individual is maintained,

and Cramer's attempt to rehabilitate it (see preceding abstract) shown to rest on obviously fallacious reasoning. W. D. R.

**Effect of Colouring Matters on some of the Digestive Enzymes.** H. W. HOUGHTON (*J. Amer. Chem. Soc.*, 1907, 29, 1351-1357).—A study of the effect of various colouring matters on the activity of pepsin has led to the following conclusions. Annatto does not affect the activity of the enzyme towards fibrin, but when present in certain proportions diminishes the activity towards egg albumin and casein. Saffron lessens the activity towards fibrin, casein, and egg albumin when it is used in the proportion of 1:800, but smaller quantities have no effect. Turmeric reduces the activity towards casein and egg albumin, but, when present in as small a proportion as 1:800, does not affect the digestion of fibrin. Carmine and Bismarck brown, when used in a smaller proportion than 1:800, do not decrease the activity of the enzyme towards fibrin, but a proportion of 1:1600 lessens the activity towards egg albumin. Crocein scarlet 1B (1:1600) inhibits entirely the action of the enzyme on fibrin, and, when present in the proportion of 1:200, diminishes the activity towards casein and egg albumin.

Annatto and oil-yellow are found to assist the hydrolysis of butter-fat by lipase, and it is therefore assumed that these colouring matters contain some lipolytically active substance. E. J. S.

**Behaviour of Hippuric Acid to Erepsin.** ORRIS GAVEN (*Zeitsch. physiol. Chem.*, 1907, 52, 526. Compare *Abstr.*, 1906, 294).—Hippuric acid dissolved in sodium hydrogen carbonate solution is not hydrolysed by erepsin. J. J. S.

**Action of the Proteolytic Ferment of *Bacillus pyocyaneus*.** EMIL ZAK (*Beitr. chem. Physiol. Path.*, 1907, 10, 287-295).—The ferment not only cleaves proteoses into simpler products, but casein is added that it also has a synthetic action both in bouillon culture and in the filtrate freed from organisms. Taylor (this vol., 1-92) has described previously a reversible action in the case of tyrosin.

W. D. R.

## Organic Chemistry.

**Synthetical Production of Optically Active Petroleum from glycerides.** JULIUS LAWKOWITZ (and HANS PICK) (*Ber.*, 1907, 40, 4141-4162).—Distillation of chaulmoogra oil with zinc dust leads to formation of gaseous products and a crude petroleum which has a characteristic odour of the higher fractions of the natural oils, and a solution is dextrorotatory. The conclusion is drawn that inactive glycerides, the activity of which is due to the constitution of the fatty acid, yield optically active hydrocarbons (compare C. Neuberg, this vol., i, 577). W. R.

**Synthesis of Optically Active Petroleum.** CARL NEUBERG (*Ber.*, 1907, 40, 4477-4478).—A claim for priority as against Lawkowitz and Pick (preceding abstract). G. Y.

**Magnesium Compounds of  $\alpha$ -Dibromopentane.** JULIUS VON LUDOWITZ (*Ber.*, 1907, 40, 4065-4066).—The author claims a prior right in the study of the action of the Grignard reagent on  $\alpha$ -dibromopentane (Bryan and Steindorff, *Abstr.*, 1905, i, 341; Grignard and Lecomte, this vol., i, 669). C. S.

**Behaviour of Various Aldehydes, Ketones, and Alcohols towards Oxidising Agents.** WILLEY DENIS (*Amer. Chem. J.*, 1907, 33, 393-394).—Evans (*Abstr.*, 1906, i, 269) has shown that the oxidation of benzoylcarbinol takes place in definite stages in accordance with the scheme put forward by Nef (*Abstr.*, 1905, i, 7). A study has now been made of the oxidation of ethyl alcohol, ethyl acetate, acetaldehyde, and acetic acid under various conditions.

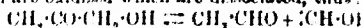
In neutral aqueous solutions of ethyl alcohol, ether, and acetaldehyde treated with  $N$  potassium permanganate, acetic acid only is evolved. In presence of excess of potassium hydroxide, however, acetaldehyde is the main product, but carbonic and oxalic acids also are evolved in quantities varying with the strength of the alkali. In all cases, the first product of the oxidation is acetaldehyde, which in presence of alkali hydroxide of greater concentration than 0.4% (compare M. Loh, this vol., i, 172) is partially converted into vinyl alcohol,  $\text{OH}\cdot\text{CH}_2\cdot\text{H} \rightarrow \text{OH}\cdot\text{CH}=\text{CH}_2$ . In presence of the permanganate, the vinyl alcohol is oxidised to glycolaldehyde, which after dissociation, thus: (a)  $\text{OH}\cdot\text{CH}_2\cdot\text{CHO} \rightleftharpoons \text{CH}\cdot\text{OH} + \text{CH}_2\text{O}$  and (b)  $\text{OH}\cdot\text{CH}=\text{CHO} \rightleftharpoons \text{CH}\cdot\text{CHO} + \text{H}_2\text{O}$ . The portion dissociated in accordance with (a) is converted into carbonic acid with intermediate formation of formic acid, and that dissociated in accordance with (b) is converted into glyoxal with oxalic acid as the final product.

When acetone is oxidised in neutral or acid solution, molecular proportions of acetic and carbonic acids are produced, and it is evident therefore that aqueous solutions of acetone do not contain any of the

compound in the enolic form. On the addition of potassium, however, the presence of *iso*acetone can be proved (1) by its quantitative conversion into mercuric *iso*acetone; (2) by its conversion into *iso*acetone alcohol, and (3) by its oxidation to carbonic and formic acids with intermediate formation of acetol.

When acetic acid is treated with alkali hydroxide, it is converted into pyruvic acid; *iso*acetic acid is not formed, since such a substance would be oxidized to oxalic acid with intermediate formation of *iso*acetol,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{OH})_2$ .

Acetol, in absence of alkali hydroxide, is oxidised to carbonic and carbonic acids, whilst, in presence of alkali, it is converted into pyruvic, hydroxypyruvic, and mesoxalic acids are successively intermediate products of the oxidation of acetol in presence of alkali. Observations have also been made with reference to the formation of lactic acid. When acetol is treated with silver oxide, carbonic and formic acids are produced, whence it is concluded that only the *ortho* isomers of acetol are oxidised which are dissociated, thus:



and  $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{C}(\text{OH})_2 + \cdot\text{CH}\cdot\text{OH}$ . With silver oxide, however, acetol is not oxidised in neutral solution. On addition of alkali hydroxide, *r*-lactic acid is produced in very small quantities of formic and acetic acids. In this case, then, only those molecules undergo oxidation which are dissociated, as follows:  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{CO}\cdot\text{CHO} + \text{H}_2\text{O}$  and



whence it is evident that pyruvaldehyde is the primary reaction product and undergoes rearrangement into *r*-lactic acid.

When a concentrated aqueous solution of mesoxalic acid is heated at 100°, the acid is converted quantitatively into glyoxylic and acetic acids. If the acid is heated at 150° with concentrated potassium hydroxide, theoretical quantities of formic and oxalic acids are produced.

Ethyl diketobutyrate is rapidly converted by solution in water with carbonate or hydroxide into methyltartronic acid. When a concentrated solution of methyltartronic acid is heated at 100°, it is decomposed into carbonic and *r*-lactic acids. On heating ethyl diketobutyrate with water at 63–65°, carbon dioxide is slowly evolved, and pyruvaldehyde and lactic and oxalic acids are formed. The latter is produced by a rearrangement of the pyruvaldehyde, the former is formed, thus:  $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et} + \text{EtOH} \rightarrow \text{CH}_3\cdot\text{CO}\cdot\text{CHO} + \text{CO}_2 + \text{EtOH} + \text{H}_2\text{O}$ . When ethyl diketobutyrate is treated with water and silver oxide, molecular quantities of acetic and oxalic acids are obtained. In presence of silver oxide, methyltartronic, oxalic, and acetic acids are produced in very small quantities of carbonic and formic acids.

**Preparation of Monochlorohydrin.** DEUTSCHE KUNSTSTOFF-FAKTIEN-GESELLSCHAFT (D.R.P. 180668).—Glycerol (100 parts) is heated with 150 parts of hydrochloric acid (sp. gr. 1.189 to 1.17) at 100° for 2 hours.

was heated in an autoclave for fifteen hours at  $120^\circ$  under a pressure of one atmosphere. The mixture, on fractionation under reduced pressure, yields first water and excess of acid, then monochlorohydrin at  $130-150^\circ$ , and, finally, the unchanged glycerol at  $160-170^\circ$ . The yield of monochlorohydrin is about 75%, and under these conditions there is no tendency for the formation of the dichlorohydrin. G. T. M.

**Butylene Chlorohydrin,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{Cl}$ .** K. KRASUSKY (*Ber.*, 1907, 145, 762-763).—The  $\phi$  butylene chlorohydrin (this vol., 1, 887) Henry (this vol., 1, 887) was obtained by the author in 1902 (this vol., 1, 425). It can be obtained by addition of hydrobromic acid to  $\phi$  butylene, prepared either by the action of alcoholic potassium butyl iodide or by withdrawal of bromine from butylene dibromide  $\text{CH}_2\text{Br}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{Br}$ , by means of zinc dust in aqueous solution.  $\phi$  Butylene chlorohydrin, when heated in a sealed tube with lime, gives methyl ethyl ketone. By prolonged shaking of the chlorohydrin with lead oxide and water,  $\delta$  dimethylethylene is formed, but by heating with lead oxide and water in a retort at  $140^\circ$  methyl ethyl ketone is produced. When prepared according to the first method, the chlorohydrin contains a small amount of the  $\alpha$  butylene chlorohydrin, revealed in the reaction with lime by production of a small quantity of aldehyde. E. H.

**By-products of the Hydrolysis of Tetramethylethylene [ $\beta$  dimethyl  $\Delta^2$  butylene] Bromohydrin.** MAURICE DELACHE (*Bull. Soc. chim.*, 1907, [iv], 1, 978-987. Compare this vol., 1, 578).—The  $\beta$  dimethyl  $\Delta^2$  butylene bromohydrin is hydrolysed by potassium hydroxide, the chief product is the hydrocarbon,  $\beta$  dimethyl  $\Delta^2$  butylene. The residue contains no appreciable quantity of alcohol, but probably consists of a mixture of isomeric acetins. The latter consist of (1) the bromide of a primary alcohol, not attacked by silver acetate, but forming an acetin when treated with potassium acetate, probably of the constitution  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{Br}$ , and (2) a bromide which, when treated with silver acetate, gives a tertiary alcohol. No asymmetric compounds are obtained, possibly owing to the ease with which the change,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{Br} \rightarrow \text{CHMe}_2\cdot\text{CHMe}_2\cdot\text{Br}$ , would be effected. E. H.

**Facts and Hypotheses concerning Isomeric Changes in Derivatives of Pinacene.** MAURICE DELACHE (*Bull. Soc. chim.*, 1907, [iv], 1, 987-995. Compare preceding abstract).—Chiefly by saturating crude  $\beta$  dimethyl  $\Delta^2$  butylene with hydrogen, and acting on the bromide formed with potassium acetate, a large proportion of an acetin, b. p.  $155^\circ$  (approx.), is obtained, which, on hydrolysis, gives an alcohol, b. p.  $141^\circ$ , but is different from the acetin boiling at the same temperature obtained by similar treatment of  $\beta$  dimethyl  $\Delta^2$  butylene. Whilst  $\beta$  dimethyl  $\Delta^2$  butylene readily combines with the haloid acids,  $\beta$  dimethyl  $\Delta^1$  butylene does not do so in the cold, and, in order to convert it completely into the chlorohydrin, the hydrocarbon must be heated at  $160^\circ$  with hydrochloric acid for fifteen days. The same amount of alcohol is formed in each case. E. H.



**Dimethylketol.** I. OTTO DIRKS and ERICH STEIN (Ber., 1907, 40, 4336—4340).—Pechmann has already described the preparation of dimethylketol,  $\text{OH}\cdot\text{CHMe}\cdot\text{COMe}$ , by the reduction of diacetyl. The authors describe a convenient method of preparing diacetyl.

von Pechmann and Dahl (Abstr., 1890, i, 1234) have described two solid modifications of dimethylketol, one with m. p.  $126^{\circ}$  and the other with m. p.  $94\text{--}98^{\circ}$ . The authors are unable to reproduce this, but find that two modifications, with the melting points  $126^{\circ}$  and  $85.5^{\circ}$  respectively, exist. These modifications are very similar in appearance, they can be crystallised without difficulty, and have the same molecular forms of dimethylketol. The difference between the compounds obtained by the authors and those obtained by von Pechmann and Dahl is ascribed to the latter authors having used ether in crystallising their compounds; it is found that the polymerised compound cannot be crystallised when ether is present.

Dimethylketol, obtained by the reduction of diacetyl with dilute sulphuric acid, was allowed to remain in a closed vessel for three and a half months, when it was transformed into a crystalline compound,  $\text{C}_4\text{H}_{10}\text{O}_3$ , with m. p.  $95.5^{\circ}$ ; that it is a dimeric form of dimethylketol was shown by a determination of its molecular weight in acetone by the ebullioscopic method.

When a little granulated zinc was added to dimethylketol which was whole immersed in a freezing mixture, the compound,  $\text{C}_4\text{H}_{10}\text{O}_3$ , was obtained as a crystalline mass, m. p.  $85.5^{\circ}$ .

Each of these modifications crystallises in rhombic habit, and their solubilities are of the same order. That they are distinguished only by the depression of the melting point, which occurs with the melting of the two.

The benzoyl derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_3$ , obtained by benzoylation of dimethylketol in pyridine solution, has b. p.  $140\text{--}141^{\circ}/8$  mm. and  $d_4^{20} = 1.076$ .

A. J. W.

**Chloromethyl Sulphate.** JOSEF HOUBEN and HANS FRIEDRICH (Ber., 1907, 40, 4306—4310).—Chloromethyl ether, prepared from hydrogen chloride and a paste of trioxymethylene and sodium acetate at  $0^{\circ}$  (compare Litterschied, Abstr., 1904, i, 962), reacts with sulphur trioxide in a freezing mixture to form chloromethyl sulphate,  $\text{CH}_2\text{Cl}\cdot\text{SO}_3\text{Me}$ , b. p.  $92^{\circ}/18$  mm.,  $D_4^{20} = 1.473$ , which is extremely reactive, and is decomposed by water, forming methylsulphate and formaldehyde, and hydrogen chloride.

$\alpha$ -Dichloromethyl ether reacts with sulphur trioxide to form  $\alpha$ -dichloromethyl sulphate, b. p.  $79\text{--}18\text{--}19$  mm., which reacts explosively with water, acetone, acetic acid, benzene, or light petroleum; the analytical results do not correspond with the formula  $(\text{CH}_2\text{Cl})_2\text{SO}_3$ .

**The Alkaline Hydrolysis of Alkyl Nitrates; a Contribution to the Constitution of Nitric Acid.** PETER KILB and CARLSON (Ber., 1907, 40, 4183—4191. Compare Abstr., 1907, i, 1000).

The presence of phenyl hydrosulphide during the hydrolysis of alkyl nitrates prevents the formation of resin; in the absence of this

the peroxide formed is converted into aldehyde, and this gives the observed result. With glyceryl trinitrate, the reaction is normal, but with the nitrates derived from monohydric alcohols in addition the sulphide is alkylated. It might be assumed that during the hydrolysis the nitrate was first reduced to nitrite, the hydrosulphide being formed as disulphide, and then that hydrolysis of the nitrite occurred, but a quantitative examination was necessary to decide between (I)  $\text{R}\cdot\text{NO}_2 + \text{KSR}^1 = \text{R}\cdot\text{S}\cdot\text{R}^1 + \text{KNO}_2$  and (II)  $\text{R}\cdot\text{NO}_2 + \text{KSR}^1 + \text{HSR}^1 = \text{R}\cdot\text{NO} + \text{KOH} + \text{R}^1\text{S}\cdot\text{SR}^1$ , (b)  $\text{R}\cdot\text{NO}_2 + \text{KOH} = \text{KNO}_2 + \text{R}\cdot\text{OH}$ .

It was found that the velocity of hydrolysis with sodium phenylmercaptide was 100 to 200 times that with alkali alone. The first step in the determination of  $\chi$ , the ratio of  $x:y$ , where  $x$  and  $y$  are the concentrations of nitrate due to reactions I and II, was the determination of  $\chi$  was found to be independent of the time, and apparently the two reactions proceed simultaneously.

By determining the concentration of the alkali, it was found that the reaction is a reaction of the second order in both cases, and the rate obtained is the sum of those due to the two reactions. The ratio of nitrate hydrolysis,  $k_n$ , to nitrite hydrolysis,  $k_{n'}$ , for various alkyls is appended:

	$K_n$	$K_{n'}$
Ethyl nitrate .....	0.0243	0.0082
n-Propyl nitrate .....	0.0160	0.0082
n-Butyl nitrate .....	0.0013	0.0078
n-Amyl nitrate .....	0.0081	0.0083

With ethyl nitrate, the hydrolysis to nitrate and phenyl methyl sulphide is almost quantitative, only 0.7% of nitrite being formed. The velocity of nitrate hydrolysis decreases rapidly as the series is extended, that of nitrite is practically constant. W. R.

**Alkaline Hydrolysis of Alkyl Nitrates in the Presence of Hydrogen Peroxide.** TOR CARLSON (*Ber.*, 1907, 40, 4191–4194, see preceding abstract).—In the hydrolysis of alkyl nitrates, the amount of nitrate and nitrite may be determined by evaporation of the unchanged alkyl nitrate in a vacuum, the residue being treated with potassium iodide and hydrochloric acid, and the nitrite determined by iron chloride. The values obtained at 70° with a nitrate concentration 0.5N, are:  $\text{CH}_3\text{NO}_2$ , nitrite, trace;  $\text{EtNO}_2$ , 10%;  $\text{PrNO}_2$ , 17%; nitrite;  $\text{i-BuNO}_2$ , 35% nitrite;  $\text{i-C}_4\text{H}_9\text{NO}_2$ , 40% nitrite. The results are not particularly accurate in consequence of the oxidising action of aldehyde. With nitrates of polyvalent alcohols the reaction velocity is greater and more nitrite is formed, glyceryl nitrate giving 67%, glyceryl dinitrate 87%, and nitrocellulose 90%. In these reactions, the alkyl complex is destroyed and cellulose, starch, and cellulose are not regenerated.

As hydrogen peroxide is formed during hydrolysis, oxygen should be evolved when hydrogen peroxide is present,  $\text{R}\cdot\text{C}_6\text{H}_4\text{O}\cdot\text{OH} + \text{H}_2\text{O}\cdot\text{OH} = \text{R}\cdot\text{C}_6\text{H}_4\text{OH} + \text{H}_2\text{O} + \text{O}_2$ , and this is proved to be the case: nitrocellulose, nitrate, oxygen and hydrated cellulose, being generated. Experimentally it gives according to theory 1 mol. of  $\text{O}_2$  for every mol. of nitrite;

this is not realised, due, perhaps, to catalytic decomposition of the alkali by alkali, and also the alcohol behaving as an "acceptor."

Benzyl nitrate and alkali phenyl sulphide give almost no reaction, but phenyl benzyl sulphide and nitrate.

**Relative Volatility of Various Groups of Acetyl Derivatives.** LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 742—764). This paper is supplementary to two already published (*Abstr.*, 1905, 1002 and 1003, and vol. 1, 674). The replacement of a hydrogen atom by an acetyl group should lower the volatility in proportion to the increase in molecular weight, but this effect is liable to be obscured by other influences. For example, (1) the position of the hydrogen atom substituted, (2) whether the hydrogen atom is attached to a carbon atom, the nature of the other groups or elements connected with the latter, and (3) the relative extents to which the molecules of the parent substance and the acetyl derivative are associated. The coefficients of association have different values, not only for compounds possessing different functions, but also for substances of the same function but containing different numbers of carbon atoms in the molecule.

A large number of tables are given in the original showing volatility relations between substances of the same type and of different acetyl derivatives, and exemplifying the effects of the several influences mentioned, and especially of the third, referred to above. The following may be quoted. Ethyl acetate boils 1° below ethyl alcohol, but difluoroethyl acetate boils 11° higher than the corresponding alcohol. The reason of this difference is found in Swarts' observations (1903, i, 222) that difluoroethyl alcohol is much less associated than ethyl alcohol. Similarly, the effect of a lower association value is caused by the replacement of hydrogen by acetyl in the SH group of capric captan, which leads to an increase of 80° in the boiling point, whereas the analogous substitution in the case of ethyl alcohol lowers the boiling point by 1°.

**[Preparation of Salts of the Iodated Higher Fatty Acids.]** FARRERFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.P. 186214). *Calcium iodobehenate*,  $\text{Ca}(\text{C}_{22}\text{H}_{43}\text{O}_2\text{I})_2$ , is most conveniently prepared in a stable condition by slowly adding an alcoholic solution of the acid to the filtered solution produced by dissolving hydrous calcium chloride in alcohol and precipitating ammonium chloride by pouring in an excess of ammonia. The organic calcium salt separates as a colourless powder, insoluble in water or alcohol. This compound may also be prepared either by double decomposition from an ammonium iodobehenate and calcium chloride or by mixing equivalent amounts of the acid and calcium hydroxide dissolved in water. Similarly, *magnesium iodobehenates*, calcium and strontium iodobehenates, *calcium iodopalmitate* were also prepared by the foregoing method, and similarly obtained as colourless, insoluble powders.

**Preparation of Iodobehenic Acid.** FARRERFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.P. 186214). Although the compound

erucic acid is not replaced by iodine on treating this substance with sodium iodides, nevertheless the corresponding bromo compound undergoes this substitution. Bromobehenic acid, obtained by replacing hydrogen bromide to erucic acid, when warmed with sodium iodide and glacial acetic acid furnishes iodobehenic acid. Other alkyl iodides may be employed instead of sodium iodide, and the solvent solvent may also be varied. G. T. M.

**Preparation of Bromo-Aliphatic Acids.** FARRENFORTH'S FORM. (U.S. PAT. & Co (D.R.-P. 186740).—It has been found that the unsaturated aliphatic acids readily combine with nascent hydrogen, and become thus converted into bromo-aliphatic acids. Thus, bromine of erucic acid, potassium bromide, and concentrated sulphuric and glacial acetic acids when shaken at a high temperature yields bromobehenic acid. Bromostearic acid was obtained by shaking and shaking a mixture of oleic acid, sodium bromide, and an aqueous solution of hydrogen chloride. G. T. M.

**Monosubstituted and Di-alkylcyanovinylacetic [Mono- and Di-alkyl- $\alpha$ -butenoic] Acids.** II. IGILIO GUARISCHI (*Mem. Accad. Sci. Torino*, 1907, [n], 57, 287—307. Compare Abstr., 1901, i, 630). The author has prepared a number of substituted  $\beta$  butenoic acids, namely: (1)  $\text{CN}\cdot\text{CH}\cdot\text{CH}\cdot\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ; (2)  $\text{CN}\cdot\text{CH}\cdot\text{CH}\cdot\text{R}\cdot\text{CH}(\text{R}')\cdot\text{CO}_2\text{H}$ ; (3)  $\text{CN}\cdot\text{CH}\cdot\text{CH}\cdot\text{R}\cdot\text{CH}(\text{R}')\cdot\text{CO}_2\text{H}$ , and (4)  $\text{CN}\cdot\text{CH}\cdot\text{CH}\cdot\text{R}\cdot\text{CH}(\text{R}')\cdot\text{CO}_2\text{H}$ , R representing an alkyl and R' an aromatic radicle. These acids are crystalline, absorb bromine, and give colorations with ferric chloride, ammonium carbonate, or with potassium nitrite. They are stored in glass vessels, the latter become coloured, owing to the alkalinity of the glass. With ferric chloride, acids of types (1) and (2) give a coloration, whilst those of types (3) and (4) do not, yielding hexa-substituted derivatives of the form:  $\text{CN}\cdot\text{CH}(\text{R})\cdot\text{CH}(\text{R}')\cdot\text{CH}(\text{R})\cdot\text{CH}(\text{R}')\cdot\text{CO}_2\text{H}$ .

**Preparation of  $\Delta^3$  butenoic acids** are prepared by the action of 60% hydrazine on (1) 3:5-dicyano-2:6-diketo-4-alkyl- $\Delta^3$ -tetrahydro- $\beta$ -butenoic acids, which are converted, by way of unstable tri-carboxylic acids, into  $\beta$ -cyano- $\beta$ -alkyl- $\Delta^3$ -butenoic acids; (2) 3 cyano-2:6-diketo-4-alkyl- $\Delta^3$ -tetrahydropyridines or 3 cyano-2:6-diketo-4:5-dialkyl- $\Delta^3$ -tetrahydropyridines, in no case was the intermediate di- or tri-carboxylic acid isolated.

**Preparation of methyl- $\Delta^3$  butenoic acid**,  $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , prepared from 3 cyano-2:6-diketo-4:5-dimethyl- $\Delta^3$ -tetrahydropyridine, crystalline in water in colourless or faintly yellow, acicular prisms, m.p. 100°C., forms a yellowish brown copper salt,  $(\text{C}_5\text{H}_7\text{O}_2\text{N})_2\text{Cu}$ , which reduces potassium permanganate or auric chloride, but does not reduce Fehling's solution.

**Preparation of methyl- $\alpha$ -ethyl- $\Delta^3$  butenoic acid**,  $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{H}$ , prepared from 3 cyano-2:6-diketo-4-methyl-5-ethyl- $\Delta^3$ -tetrahydro-

pyridine, crystallises from water in colourless, prismatic, short prisms, m. p. 175—176°.

*γ*-Cyano- $\alpha$ -methyl- $\beta$ -ethyl- $\Delta^2$ -butenoic acid,  
 $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{Et})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ ,

prepared from 3-cyano-2:6-diketo-3-methyl-4-ethyl- $\Delta^2$ -tetrahydropyridine, has m. p. about 206°.

*γ*-Cyano- $\beta$ -propyl- $\Delta^2$ -butenoic acid,  $\text{CN}\cdot\text{CH}\cdot\text{CPr}^n\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3:5-dicyano-2:6-diketo-4-propyl- $\Delta^2$ -tetrahydropyridine, the ammonium derivative of its enolic form, crystallises from alcohol in prisms or needles, m. p. 225—227° (decomp.).

*γ*-Cyano- $\beta$ -isopropyl- $\Delta^2$ -butenoic acid,  $\text{CN}\cdot\text{CH}\cdot\text{CPr}^i\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3:5-dicyano-2:6-diketo-4-isopropyl- $\Delta^2$ -tetrahydropyridine, forms crystals, m. p. 177—178°.

*γ*-Cyano- $\beta$ -methyl- $\alpha$ -propyl- $\Delta^2$ -butenoic acid,  
 $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHPr}\cdot\text{CO}_2\text{H}$ ,

prepared from 3-cyano-2:6-diketo-4-methyl-5-propyl- $\Delta^2$ -tetrahydropyridine, crystallises from water in colourless or faintly yellow, acicular prisms, m. p. 154—155°, and forms a crystalline salt,  $\text{C}_9\text{H}_{13}\text{O}_2\text{NEt}_2$ .

*γ*-Cyano- $\beta$ -hexyl- $\Delta^2$ -butenoic acid,  $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_{13})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3:5-dicyano-2:6-diketo-4-hexyl- $\Delta^2$ -tetrahydropyridine, m. p. 175—180°.

*γ*-Cyano- $\beta$ -phenyl- $\Delta^2$ -butenoic acid,  $\text{CN}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3-cyano-2:6-diketo-4-phenyl- $\Delta^2$ -tetrahydropyridine, the ammonium salt of 3:5-dicyano-2:6-diketo-4-phenyl- $\Delta^2$ -tetrahydropyridine, crystallises from alcohol in colourless or faintly yellow plates, m. p. 256—257°.

*γ*-Cyano- $\beta$ -m-tolyl- $\Delta^2$ -butenoic acid,  $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from the ammonium salt of 3:5-dicyano-2:6-diketo-4-m-tolyl- $\Delta^2$ -tetrahydropyridine, crystallises from acetic acid in heavy, colourless or faintly yellow prisms, m. p. 255—257°.

*γ*-Cyano- $\beta$ -cumyl- $\Delta^2$ -butenoic acid,  $\text{CN}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Pr}^n)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from 3:5-dicyano-2:6-diketo-4-cumyl- $\Delta^2$ -tetrahydropyridine, separates from alcohol in crystals, m. p. 240°.

*γ*-Cyano- $\alpha$ -benzyl- $\beta$ -methyl- $\Delta^2$ -butenoic acid,  
 $\text{CN}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ ,

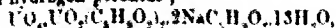
prepared from 3-cyano-2:6-diketo-4-methyl-5-benzyl- $\Delta^2$ -tetrahydropyridine, forms colourless crystals, m. p. 156—157°.

*γ*-Cyano- $\beta$ -ethyl- $\Delta^2$ -butenoic, *γ*-cyano- $\beta$ -isobutyl- $\Delta^2$ -butenoic, and *γ*-cyano- $\beta$ -isopropyl- $\Delta^2$ -butenoic acids, and *γ*-cyano- $\beta$ -methyl- $\alpha$ -allyl- $\Delta^2$ -butenoic acids have also been obtained in small quantities, but have not been analysed.

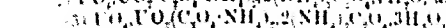
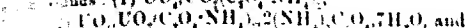
**Complex Salts of Uranium Peroxide.** ARBOLD, MANN, and FERRUSO BIANCHI (*Atti R. Acad. Lincei*, 1907, ii, 576—584. Compare this vol., ii, 54).—The following salts of uranium peroxide, prepared by the authors, are yellow or yellowish yellow in colour, and are decomposed by water with precipitation of uranium peroxide.

$\text{UO}_4\cdot\text{UO}_2(\text{OAc})_2\cdot 2\text{NH}_4\cdot\text{OAc}$  was obtained by the interaction of uranium nitrate, ammonium acetate, and hydrogen peroxide.

by the interaction of uranyl and barium acetates, and hydrogen peroxide;



sodium uranyl nitrate, sodium valerate, and hydrogen peroxide; the compounds are:

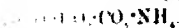
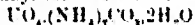


sodium uranyl oxalate, ammonium oxalate, and hydrogen peroxide. The compound formed by sodium uranyl

peroxide and hydrogen peroxide is obtained as a yellow precipitate, and is purified or analysed.

Sodium uranyl nitrate, chloride, sulphate, &c., hydrogen peroxide and acid-soured liquids, but the compounds formed could not be analysed.

With sodium uranyl pyrophosphate, the compound  $\text{Na}_2\text{P}_2\text{O}_7 \cdot 18\text{H}_2\text{O}$  or  $[\text{NaO} \cdot \text{UO}_2 \cdot \text{O} \cdot \text{PO}(\text{ONa})_2]_n \cdot \text{O}$  (1) is obtained, and ammonium uranyl carbonate the compound



T. H. P.

#### Complex Salts of Iridium. Irido oxalates. CESARE GIALDINI

*Atti dell. Lincei*, 1907, [v], 16, ii, 551–561).—When a solution of iridium chloride or an alkaline iridichloride is treated with excess of

sodium hydroxide, the principal reaction, represented by:  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O} + 4\text{KOH} = \text{IrO}_2 + 4\text{KCl} + 2\text{H}_2\text{O}$ , is accompanied by secondary reactions expressed by the equations:  $2\text{IrCl}_3 + 7\text{KOH} = \text{Ir}_2\text{O}_3 + 7\text{KCl} + 3\text{H}_2\text{O}$ ,  $\text{HClO} + \text{KOH} = \text{KCl} + \text{H}_2\text{O} + \text{O}$ ;  $\text{Ir}_2\text{O}_3 \cdot \text{Aq} + \text{O} = \text{IrO}_2 \cdot \text{Aq}$ .

Hence, in order to prevent the ready decomposition of the  $\text{Ir}(\text{OH})_3$ , it is necessary to limit as far as possible the formation of  $\text{Ir}(\text{OH})_3$  and  $\text{Cl}^-$  by the reaction:  $\text{Ir}(\text{OH})_3 + \text{Cl}^- \rightleftharpoons \text{Ir}(\text{OH})_2 + \text{HClO}$ . By adding hypochlorous

acid, it is possible to displace the equilibrium of this reaction to the left, and so facilitate the precipitation of iridium hydroxide, the preparation and separation of which usually occupy several

days. The reaction of oxalic acid on iridium dioxide takes place in two stages:  $\text{IrO}_2 + \text{H}_2\text{C}_2\text{O}_4 = \text{Ir}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{CO}_2$  and  $\text{Ir}_2\text{O}_3 + 6\text{H}_2\text{C}_2\text{O}_4 =$

$\text{K}_2\text{IrC}_2\text{O}_6 + 3\text{H}_2\text{O}$ , for the completion of which it is necessary to allow the reaction for thirty to thirty five hours. Potassium sesquioxalate  $\text{K}_2\text{IrC}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ , prepared by neutralising the acid with

potassium carbonate, separates from water in pale orange-yellow crystals. [Zambonini,  $\alpha:b:c = 0.7319:1:0.9565$ ;  $a = 88.3137^\circ$ ,  $b = 107.11^\circ$ , and  $\gamma = 57.118^\circ$ ].

T. H. P.

#### Oxymethylenecamphor and Mesityloxidoxalic Esters.

See *Reviews (Annalen*, 1907, 356, 251–280).—Willicensen's

ketonene compounds (Abstr., 1896, i, 552; 1900, i, 9) had

observed that solvents with slight dissociating powers and

dissociating solvents favour the formation of the enolic form of

these compounds, whilst the ketonic form is stable in strongly

dissociating solvents. This rule, however, does not hold good for all

these substances. Two exceptions, oxymethylenecamphor and

mesityloxidoxalic ester, have been studied spectrometrically (Abstr., 1899, ii, 735). The present author has investigated the behaviour of the same substances by Wislicenus's ferric chloride colorimetric method (Abstr., 1900, i, 9). The results of these experiments with mesityloxidoxalic ester and mesityloxidoxalic  $\alpha$ -methyl-necampbor confirm Brühl's statement (*loc. cit.*) that this substance has the ketonic constitution and that enolic transformation does not take place either in feebly or strongly dissociating solvents.

$\beta$ -Mesityloxidoxalic esters do not give a coloration with ferric chloride in ether, benzene, or chloroform solution, but after exposure to light give a slight coloration in ethyl- or methyl-alcoholic solution. On the other hand, the enolic or  $\alpha$ -esters undergo the ketonic transformation rapidly in methyl- or ethyl-alcoholic, but only slowly in benzene, benzene, and most slowly in chloroform solution. In the case of the  $\beta$  esters slowly polymerise, the polymerisation being accelerated by exposure of the solution to light. In consequence of the rapid ketonic transformation, the  $\alpha$  esters yield the same polymeride in the above solvents with the exception of chloroform. The ketonic transformation of the  $\alpha$ -esters and the polymerisation of the  $\beta$  esters do not take place completely even on prolonged action of the light, the converse transformation from the polymeride could not be observed. The propyl and amyl esters polymerise more slowly than the ethyl and ethyl mesityloxidoxalates.

The *polymeride* of ethyl mesityloxidoxalate,  $(C_{10}H_6O_4)_n$ , after eight days, separates in monoclinic crystals [ $a:b:c = 1.562:1.000:1.143$ ], m. p. 175°, sublimes unchanged, is less soluble than the  $\beta$ -ester, and does not give a coloration with ferric chloride.

The *polymeride* of methyl mesityloxidoxalate,  $(C_9H_6O_4)_n$ , after ten to twelve days, separates in monoclinic crystals [ $a:b:c = 1.0319:1.1761$ ;  $\beta = 91.54^\circ$ ], m. p. 225°, and has properties similar to those of the polymeride of the ethyl ester. A polymeride of  $(C_9H_6O_4)_n$ , m. p. 236—237° (partial decomp.), which resembles the solid  $\beta$  methyl ester is exposed to diffused light for eight days.

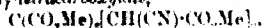
*Propyl mesityloxidoxalate*, prepared by the action of propyl mesityl oxide and propyl oxalate in ethereal solution, is obtained as a yellow oil, b. p. 120—130°/20 mm., which gives a strong ferric chloride reaction with ferric chloride. The  $\alpha$ -ester forms a green, crystalline copper salt,  $(C_{11}H_8O_4)_2(Cu.H_2O)$ , from which it is liberated by treatment with concentrated dilute sulphuric acid. The *polymeride*,  $(C_{11}H_8O_4)_n$ , after 60 days, forms in ninety days, sublimes with partial decomposition, and does not give a ferric chloride reaction.

*Amyl mesityloxidoxalate*, prepared from amyl oxalate, is obtained as a yellow oil, b. p. 100—130°/20 mm., gives a strong ferric chloride reaction, and forms a green, crystalline copper salt,  $(C_{13}H_{10}O_4)_2(Cu.H_2O)$ , which loses  $H_2O$  at 115°; m. p. 129—130°. The  $\alpha$ -ester is liberated from the copper salt as a viscid, yellow oil. The *polymeride*,  $(C_{13}H_{10}O_4)_n$ , formed in one hundred and twenty days, separates from benzene solution in crystals, m. p. 113—114°.

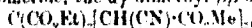
**Preparation of Methyleneclitryl Halides.** F. S. KILPATRICK, FORM. FRIEDR. BAYER & Co. (D.R.-P. 186659) = Methyleneclitryl halides.

an unstable substance, which cannot be converted into its bromide by means of either phosphorus trichloride or trichlorobromide or the corresponding oxyhalide. It has now been found that the conversion may be readily effected by means of phosphorus pentachloride or pentabromide. Methylenechloric acid (1 part) is mixed with 4 parts of phosphorus pentachloride, hydrogen chloride is evolved, phosphorus trichloride produced is distilled off, whilst the *methylenechloric anhydride*,  $\text{CH}_2 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}$ , colourless prisms, m. p. 100°, crystallised from benzene or chloroform with the addition of phosphorus pentachloride. *Methylenecitric bromide*, a viscid oil, is obtained when phosphorus pentachloride is replaced in the foregoing experiment by 4 parts of phosphorus pentabromide. The alkali metal chlorates may be employed in these reactions in place of the phosphorus pentachloride. G. T. M.

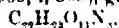
**Condensation of the Esters of Mesoxalic or Oxalacetic Acid with the Esters of Cyanoacetic Acid.** CH. SCHMITT (*Ann. Chim. Phys.*, 1907, (vi), 12, 406—432).—Mainly a resume of work already published (compare Abstr., 1905, i, 508; 1907, i, 112), but the following compounds are described for the first time. *Methyl  $\alpha$ -cyanoacetic  $\beta$ -tetracarboxylate*,



m. p. 120°, prepared by the action of methyl mesoxalate on excess of methyl cyanoacetate, yields the *compound*,  $\text{C}_{12}\text{H}_{12}\text{O}_{11}\text{N}_2$ , m. p. 115°, on treatment with alcoholic hydrogen chloride;  *$\beta$ -dimethyl  $\alpha$ -diethyl  $\alpha$ -cyanoacetic  $\beta$ -tetracarboxylate*,  $\text{C}(\text{CO}_2\text{Me})_2[\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$ , m. p. 125°, is similarly obtained from methyl mesoxalate and ethyl cyanoacetate, its isomeride, the  $\alpha$ -dimethyl  $\beta$ -diethyl ester,

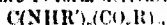


m. p. 120°, described (Abstr., 1905, i, 508), gives the compound,

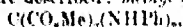


m. p. 127°, when treated with alcoholic potassium hydroxide.

The esters of mesoxalic acid condense with certain aromatic amines at ordinary temperature to form derivatives of the type:



two of the following are described: *methyl bisanilinomoxalate*,



m. p. 113°, *ethyl bisanilinomoxalate*,  $\text{C}(\text{CO}_2\text{Et})_2(\text{NHPh})_2$ , m. p.

117°, and *methyl bis-o-toluidinomoxalate*,  $\text{C}(\text{CO}_2\text{Me})_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)_2$ , m. p. 117°. M. A. W.

**Additive Compound of Two Dicarboxyglutaconic Ester Radicals.** MAX GUTHEIT [and ERNST HARTMANN] (*Ber.*, 1907, 40, 1000). In the course of a study of the halogen derivatives of ethyl dicarboxyglutaconate, a crystalline compound,  $\text{C}_{20}\text{H}_{22}\text{O}_{16}$ , m. p. 86°, has been obtained by heating ethyl bromodicarboxyglutaconate with ethyl dicarboxyglutaconate in xylene solution. This compound, which is formed also in a 90% yield by the action of iodine on ethyl dicarboxyglutaconate in toluene solution, or by prolonged boiling of the corresponding derivative of the ester with finely divided sulphur in



benzene, reacts readily with alcoholic sodium ethoxide. Its behaviour towards bromine, alkaline permanganate, and glacial acetic acid shows that it does not contain an ethylene group.

**Preparation of Thioglycollic Acid from Chloroacetic Acid.** KATZ & CO. (D.R.P. 180875).—When chloroacetic acid is added to an alkaline solution with sodium sulphide and sulphur, a disulphide is produced, and this substance on reduction either with sodium or hydrogen sulphide furnishes thioglycollic acid,  $\text{HS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

**Deaminocystine and Aminoethyl Disulphide.** G. KATZ and ERICH ASCHER (*Biochem. Zeitsch.*, 1907, 5, 451).—The gentle action of nitrous acid on cystine, a hydroxy- $\beta$ -disulphide,  $\text{S}_2(\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H})_2$ , can be obtained in the form of a salt;  $[\alpha]_D^{20} = 19.08^\circ$ . By precipitation of the latter with nitric acid, the disulphide is obtained in solution;  $[\alpha]_D^{20} = 19.08^\circ$ . On distillation, cystine loses carbon dioxide and yields a small quantity of aminoethyl disulphide,  $\text{S}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$ , which can be obtained in the picrate, m. p.  $197^\circ$ .

**Conversion of Methyl Alcohol into Formaldehyde and Preparation of Formalin.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 30, 1023–1044. Compare this vol., i, 892).—The experiments were performed either in the apparatus described previously in a slightly simplified form of it. The following catalysts are energetic, but produce chiefly carbon dioxide and monoxide, and oxygen, the quantity of formaldehyde in the product being slight: asbestos containing (1) freshly-reduced powdered copper, a mixture of cerium sulphate and thorium oxide; (3) platinum. With coke coated with reduced copper, 39.78% of alcohol was converted directly into formaldehyde, whilst, with metallic platinum, the catalyst is changed. Contrary to the statement of Sabatier and Senderens, the former substance hardly acts as a catalyst at all, even at  $200^\circ\text{C}$ . when methyl alcohol is passed over it without admixture of air.

The reaction is exothermic, 31.1 Cal. being evolved for each gram molecule of methyl alcohol converted into formaldehyde. Consequently if the reaction is once started, it should, under favourable conditions, proceed without any further application of energy. A method, which can also be applied technically, has been devised, and 42% of methyl alcohol can thus be transformed. Freshly reduced copper gauze is employed as catalyst; this must not contain more than 1% of acetone. With platinum and filings as catalysts, the yields are unsatisfactory. When methyl alcohol without admixture of air is passed over heated iron, the products obtained are carbon monoxide and dioxide, hydrocarbon, and methane, carbon, very small quantities of formaldehyde, and possibly  $(\text{CH})_2\text{O}$ , the constitution of which has not yet been determined; with iron it may form  $\text{Fe} \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{O} \end{array}$ , which on heating decomposes forming  $\text{Fe} + \text{CO} + \text{C}$ .

percentage composition of the gases depends on the strength of the acid employed and the rate of passage of the alcohol vapours over the acid.

Z. K.

**Metacetaldehyde.** ARTHUR HANTZSCH and J. OENIGLIN (*Ber.*, 1907, 40, 4341—4344).—Metacetaldehyde has hitherto been considered by the majority of those who have investigated it as stereoisomeric with paracetaldehyde, and accordingly to be a termolecular compound of paracetaldehyde. The authors are led to the following conclusions. Metacetaldehyde exists in one form only; when pure, it is quite stable and is not changed when dissolved in phenol, that is, acetaldehyde is not formed. Metacetaldehyde is not termolecular, but is termolecular in phenol solution; in thymol solution, it is probably monomolecular. From these results, it is certain that metacetaldehyde is isomeric with paracetaldehyde.

A. McK.

**Action of Magnesium Hydroxide on Chloral Hydrate.** JOSEF ROSENTHALER and R. REIS (*Chem. Zentr.*, 1907, ii, 891; *Monat. Zeit.*, 1907, 22, 678—679).—Chloroform is not decomposed when heated with magnesium hydroxide on a water-bath. Chloral hydrate when similarly treated is decomposed chiefly into formic acid and formic acid, but at the same time a secondary reaction takes place whereby a greater proportion of magnesium hydroxide is consumed, carbon monoxide and magnesium chloride also being formed. The action of magnesium hydroxide on chloral hydrate can therefore be employed in the quantitative estimation of the chloral hydrate.

W. H. G.

**Stability of Bisulphite Compounds of Aldehydes and Ketones.** JOHN B. CORROCK (*Chem. News*, 1907, 93, 225).—It has been observed that when aldehydes or ketones are treated with the bisulphite solution prepared by saturating sodium carbonate solution with sulphur dioxide, the bisulphite compounds do not separate. Experiments have been carried out which show that this is due to the stability of the compounds in sulphurous acid, and it has been found that separating the bisulphite solutions from sodium carbonate the sulphurous acid should only be passed into the solution until a very faint turbidity appears.

E. G.

**Preparation of Formaldehydesulphoxylates.** FRIEDWILHELM MEYER, LECTURER, & BRUNO (D.R.P. 180832. *Compte Rend.*, 1907, ii, 400).—Acetone and its homologues react with bisulphites to form crystallisable ketonesulphoxylates. A saturated solution of acetone is saturated with sulphur dioxide and is then treated in the cold with zinc dust, the temperature being raised to 50—60°. After cooling, the solution deposits a ketonesulphoxylate, which is converted into the sodium salt by treatment with sodium carbonate. The sodium acetonesulphoxylate in aqueous solution in water with aqueous formaldehyde is readily changed to formaldehydesulphoxylate, whilst the acetone is eliminated.

G. T. M.

**Combined Sulphurous Acids. II.** WILHELM KRAEP AND E. BACH (*Chem. Zentr.*, 1907, ii, 970-971; from *Arch. Kunt.*, 1907, 20, 231-258. Compare Abstr., 1904, i, 715). It is shown that formaldehyde-sulphurous acid and acetaldehyde-sulphurous acid are both strong acids, and it is therefore highly probable that sulphurous acids of benzaldehyde, acetone, and arabinose are strong acids. This could not be proved, however, by conductivity measurements, because of the high degree of dissociation of the complex in water. As a rule, the degree of dissociation of the complex is greater in an acid solution than in a neutral solution, which it follows that the dissociation of the non-ionised acid is less than that of the anion. The rate of dissociation of the anion is, however, diminished by the presence of an acid.

The addition of acetaldehyde to an aqueous solution of sodium hydrogen sulphite diminishes the degree of dissociation of the complex in agreement with the law of mass action. The dissociation of the complex increases with a rise of temperature.

*Chloral sodium hydrogen sulphite*,  $\text{CCl}_3\cdot\text{CHO}\cdot\text{HSO}_3\text{Na}$ , crystalline form by passing sulphur dioxide into a solution of sodium carbonate to which is added a solution of chloral hydrate. The latter compound, decomposed to a high degree in aqueous solution.

W. B.

**The Ammonia Reaction for Distinguishing between Enols and Ketonic Derivatives.** ARTHUR MICHAEL AND HANSEN (*Ber.*, 1907, 40, 4380-4388. Compare Hantzsch and Duffin, *A.*, 1902, i, 223, 675; Hantzsch, this vol., i, 927).—The authors discuss this reaction by inquiring (1) how far the assumption is correct that the reaction  $\text{CH}_3\cdot\text{CO}\cdot + \text{NH}_3 \rightarrow \text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{NH}_2$  is slow with subsequent formation  $\text{CH}_3\cdot\text{C}(\text{OH})\cdot + \text{NH}_3 \rightarrow \text{CH}_3\cdot\text{C}(\text{ONH}_2)_2$ , and also intramolecular change  $\text{CH}_3\cdot\text{CO}\cdot \rightarrow \text{CH}_3\cdot\text{C}(\text{OH})\cdot$  takes place at measurable velocity; (2) if there really exists a sharp difference between the solvents, chloroform, benzene, and toluene, on the one hand, and ether, on the other; (3) whether all real acyclic compounds give instantaneously stable insoluble ammoniacal compounds, does benzoic acid.

It is found that, in general, enols react more easily than ketones, there are exceptions, for instance, acetylacetone and the ketone diacetoacetate, the former gives the ammonia compound,  $\text{CH}_3\cdot\text{C}(\text{ONH}_2)_2$ , stable at 54 m. p. 65-67°, at once on mixing a toluene solution of 4 ammonia in toluene, or at -10° with ether, carbon tetrachloride, or toluene solutions. The reaction velocity does not depend on the structure, but also on the "chemical potential" of the reacting compounds.

Triethylamine when mixed with either the ketone or the enolification of dibenzoylmethylmethane in acetonitrile or ethyl alcohol solution at -10° gives instantaneously the yellow colored compound with the same intensity in either case. Inasmuch as the enol isomeride is fairly stable in these media, the conclusion is that the ketonic  $\rightarrow$  enolic change takes place practically instantaneously.

The authors cannot confirm the alleged difference between chloro-

sometimes precipitation occurs more quickly in toluene than in benzene; sometimes in ether: the speed of precipitation depends, not only on the solubility and insolubility of the ammonium salt, but also on the degree of supersaturation, as, when experiments are carried out with acetylacetone, the additive product is at once precipitated, whereas at  $-5^{\circ}$  there is a decrease in the velocity with increasing solution.

The case of benzoic acid ( $k$  0.0060) as a typical acid is criticised by acylacetic acid ( $k$  0.0055) of approximately the same strength. Benzoic acid is treated with ammonia in benzene, precipitation of salt is instantaneous; 0.0025 of acid in 5 c.c. dry benzene with 0.001 of ammoniacal benzene takes four minutes at  $15^{\circ}$  before precipitate appears, although the solubility of salt is 1 in 15,000.

In the case of acetic acid, ammonia does not at once produce a precipitate when the acid is in excess, although ammonium acetate is soluble. This is explained by assuming the formation of a soluble complex salt.

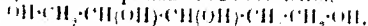
The "ammonia reaction" cannot therefore be used to distinguish ketonic and ketonic compounds.

Acetative compounds with phloroglucinol, dimethyldihydroxyacetone and dimethyldihydroxyresorcin have m. p.'s  $88-91^{\circ}$ ,  $130^{\circ}$ , and  $130^{\circ}$ , respectively. W. R.

**Decomposition of Pentaerythritol Tetraformate on Heating.** J. VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 10, 165-168).—The ease with which  $\Delta^{\circ}$  hexatriene is formed by van Romburgh and van Dorssen, *Abstr.*, 1906, i, 722) by heating divinylglycol formate has led to a study of the decomposition of esters of polyhydric alcohols.

Pentaerythritol tetraformate, m. p.  $57^{\circ}$ , does not decompose in the liquid phase as divinylglycol formate, but, on heating at  $220-230^{\circ}$ , divinylacetylene is evolved and pentaerythritol regenerated. E. G.

**Derivatives of the  $C_5$  Sugars from Meta- and Para-oximes.** HEINRICH KILIANI and A. SAUTERMEISTER (*Ber.*, 1907, 40, 4226). Compare *Abstr.*, 1904, i, 373).—Although meta- and para-oxime acids are entirely different in constitution, their barium salts crystallise together, and the quinine salts show almost identical melting points and solubility. The corresponding  $C_5$  sugars obtained from them are different, but their oximes have almost identical melting points. The oxime of pentaene-3:4:5-triol (metasaccharopentose) is a prismatic crystal, less soluble than sodium chloride, m. p.  $156^{\circ}$ ,  $[\alpha]_D^{20} + 10.6^{\circ}$ ; the oxime of pentaene 1:4:5 triol 3 one (paracaccharopentose) has m. p.  $136-137^{\circ}$ ,  $[\alpha]_D^{20} + 11.8^{\circ}$ . The pentaene oxime is readily reduced to pentaene 1:2:3:5-tetrol.



is reduced by sodium amalgam; the use of calcium (Neuberg and Marx, *Ber.*, 1906, 39, 87) for this purpose being unsuccessful. The tetrol is a solid, its tetrabenzosalt forms glistening needles, m. p.  $85-86^{\circ}$ , and like benzoyldextrose, is resistant towards acids or alkalis at  $100^{\circ}$ , but readily hydrolysed by sodium ethoxide. The tetrol is a hygroscopic syrup;  $[\alpha]_D^{20} + 29^{\circ}$ . E. F. A.

**Combined Sulphurous Acids. III. Dextrose Sulphuric Acid.** WILHELM KEMP and EMIL RAUB (*Chem. Zentr.*, 1907, from *Arb. Kaiser. Ges.-A.*, 1907, 23, 269—296. Comp. Rend., 1910).—Two optically active stereoisomeric compounds, which are not mirror images of one another, are obtained by the interaction of sodium hydrogen sulphite and dextrose. The compound obtained up to the present is the less soluble salt; it is levorotatory, but gradually changes in solution into the other isomeride until equilibrium is established, the solution then being dextrorotatory. From conductivity measurements, it follows that the free acid is a very strong acid. The dissociation of the complex anion is not decreased by the addition of dextrose, whereas the effect is an increase in the number of hydrogen sulphite ions is a small degree of dissociation of the complex in an acid solution is greater than in a neutral solution, neither does it increase to a great extent with a rise of temperature. The diminution of degree of dissociation of the complex produced by the addition of dextrose is very great. The addition of acetaldehyde to an aqueous solution of dextrose sulphurous acid results in the formation of a dextrose sulphurous acid and the liberation of dextrose. W. R.

**The Hydrolysis of Sugars.** ROBERT J. CALDWELL (*Brit. Assoc. Report*, 1906, 76, 267—292).—The report contains an introduction and summary of the different conditions under which sugars are hydrolysed. The various theories put forward to account for the inverting action of acids are discussed, and the facts in favour of the addition theory are set forth in some detail. The report contains a complete bibliography, and the matter which is arranged in a logical sequence in each section is dated systematically throughout. W. R.

**Diastasic Liquefaction of Starch.** AUGUSTE FRIEDLÉ and JULES WOLFF (*Compt. rend.*, 1907, 145, 261—263).—The liquefaction of starch is subject to the same influences as those observed under pressure (Abstr., 1906, i, 803, 804). N. R.

**The Present Position of the Chemistry of the Cobalt.** HENRY H. ROBINSON (*Brit. Assoc. Report*, 1906, 76, 227).—A summary of the investigations made on the nature of different cobalt compounds. W. R.

**Complex Metal Ammonias. IV. Tetraethylenediamine-di-aquo-tetra-cobaltodibromide Salts.** ALFRED WEISS and GUSTAV JANTSCH (*Ber.*, 1907, 40, 4126—4134. Comp. Rend., vol. i, 482).—The salts obtained by the action of tetraethylenediamine on aqueous solutions of cobaltous salts in the presence of bromine and diamine are found on investigation, excluding water and acid, to have the composition  $(Co_4En_4)X_n$ , where  $En$  = ethylenediamine and  $X$  = a univalent acid radicle. When treated with cold hydrochloric acid, no halogen is evolved, but 1 mol. of the salt yields 1 mol. of cobaltous salt and 2 mols. of a cis-diaquodiethylenediamine complex.

$[(\text{OH})_2\text{CoEn}_2]\text{X}$ . The  $\text{H}_2\text{O}$  mols. in the 3 mols. of the diaquo-salt are present as such in the parent substance, since these complexes do not react like diaquo-salts; however, the complex of the compound contains 4 atoms of oxygen, which must be present as hydroxyl groups; consequently two  $[(\text{OH})_2\text{CoEn}_2]\text{X}$  residues must be present in the building up of the molecule. Since the molecule is decomposed by hydrochloric acid as stated above, it follows that these compounds are formed by the combination of 1 mol. of a cobalt salt with 2 mols. of a dihydroxodiethylenediaminecobalt complex,  $[(\text{OH})_2\text{CoEn}_2]\text{X}$ . They, however, contain, in addition, 2 mols. of water retained by them in the dried state (the function of which is not yet known), and, as in solution the whole of the acid is evolved, the following constitutional formula is assigned to them, which are consequently named *tetraethylenediamine-ethylenedibutylcobaltic salts*,  $\left\{ \text{Co} \begin{pmatrix} \text{H}_2\text{O} \\ (\text{HO})_2\text{CoEn}_2 \end{pmatrix} \right\}_2 \text{X}_2$ .

It is pointed out that cobaltous-cobaltic hydroxide,  $\text{Co}_2(\text{OH})_6$ , has a similar constitution.

A solution of cobalt chloride containing ethylenediamine yields, on exposure to the air and subsequent treatment with common salt, a precipitate containing the *chloride* of the series and triethylenediaminecobaltic chloride. The latter compound is removed by treating the precipitate with water, leaving the former as a bright red, slightly blue powder. This is converted by sodium sulphate into the *sulphate*,  $\left\{ (\text{SO}_4)_2 \cdot 5\text{H}_2\text{O} \right\} (\text{Co}_2\text{En}_2)_2$ , crystallising in bright red, microcrystals.

A solution of cobalt sulphate containing ethylene-diamine deposits, on exposure to the air, the sulphate in the form of a precipitate. It cannot be recrystallised, being sparingly soluble in water. When treated with barium chloride and then with sodium chloride, a *sulphate* similar to the above, but containing  $7\text{H}_2\text{O}$ , is obtained. The following salts are similarly obtained from the chloride of the composition: *dithionate*,  $\text{Co}_2\text{C}_4\text{H}_{12}\text{O}_8\text{N}_4\text{S}_6 \cdot 2\text{H}_2\text{O}$ , a bluish-white *platinichloride*,  $\text{Co}_2\text{C}_4\text{H}_{12}\text{O}_8\text{Cl}_2\text{Pt}_2 \cdot 2\text{H}_2\text{O}$ , a light brownish-yellow powder; *iodide*,  $\text{Co}_2\text{C}_4\text{H}_{12}\text{O}_8\text{N}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ , a brownish-yellow powder.

W. H. G.

**Action of Ammonia on the Oxides and Chlorohydrins of Ethylene and Tetramethylethylene [ $\beta$ -Dimethyl- $\Delta^2$ -butylene].** See also L. DUDA (*J. Russ. Phys. Chem. Soc.*, 1907, 30, 1175). The tendency of  $\alpha$ -olefins to combine with ammonia does not depend so markedly on the structure of the olefin as the case with its tendency to combine with water, inasmuch as the former tendency does depend on the structure of the olefin, it is the reverse of that of its combination with water. The products obtained by the action of ammonia on the chlorohydrins of ethylene and  $\beta$ -dimethyl- $\Delta^2$ -butylene are the corresponding *amides*, which are formed at quite low temperatures; actually, in the formation of a hydroxy-amine, the oxides are the only intermediate products, and probably the whole of the reaction.

the  $\alpha$ -hydroxy-amine formed from  $\alpha$ -monochlorohydrin reacting with the amine obtained from the corresponding  $\alpha$ -oxide.

$\alpha$ -Hexylene oxide is formed by heating hexylene with  $\text{CaH}_2$  powder, and is best purified with 1% aqueous potassium permanganate. With aqueous ammonia in a sealed tube at  $100^\circ$ , the hexylene yields: (1) a secondary hydroxy-amine,  $(\text{C}_6\text{H}_{11}\text{O})\text{NH}_2$ , b. p.  $189.5-190.5/750$  mm. (lit.  $189.5-190.5/750$  mm.), (2) hexylamine,  $\text{NH}_2\cdot\text{C}_6\text{H}_{13}\cdot\text{OH}$ , b. p.  $189.5-190.5/750$  mm. (lit.  $189.5-190.5/750$  mm.), which behaves as an alkali towards many reagents, and is also formed under similar conditions by hexylene chlorohydrin, platinichloride, hydrochloride, and carbonate have been obtained in impure form. With nitrous acid, the  $\alpha$ -amine yields the same as  $\alpha$ -hexylene glycol.

$\beta\gamma$ -Dimethyl- $\Delta^2$ -butylene oxide was obtained by heating the corresponding chlorohydrin over potassium hydroxide. From the  $\alpha$ -amine, the oxide or chlorohydrin must be heated with excess of aqueous ammonia at  $100^\circ$ . The amine,  $\text{NH}_2\cdot(\text{C}_6\text{H}_{13})_2\text{OH}$ , b. p.  $162-164/756$  mm., solidifies below  $0^\circ$ , and melts at  $0-1^\circ$  (lit.  $0-1^\circ$ ), readily absorbs carbon dioxide, forming a crystalline hydrate,  $(\text{C}_6\text{H}_{13})_2\text{N}\cdot\text{CO}_2\cdot\text{H}_2\text{O}$ , m. p.  $30-32^\circ$ , which is also formed when the moist amine is mixed with water. On desiccation, the hydrate returns into the liquid amine. With the dry amine, nitrous acid yields pinacolone, but chiefly pinacone.

**Choline Cadmium Chloride.** FRIEDRICH W. SCHMIDT (*Zeitsch. physiol. Chem.*, 1907, 53, 428).—*Choline cadmium chloride*,  $\text{C}_5\text{H}_{14}\text{ONCl}_2\text{CdCl}_2$ ,

is recommended as a substitute for the platinichloride in the precipitation and purification of choline. It is thrown down as a white precipitate on the addition of an alcoholic solution of potassium chloride to an aqueous solution of choline chloride.

**The Chemistry of Bile. II. Affinity Constant of Glycolic Acid.** SAMUEL BOND (*Zeitsch. physiol. Chem.*, 1906, 50, 13).—Pure glycolic acid (Abstr., 1906, i, 633) is a relatively strong acid. The dissociation constant, calculated from results of electrical conductivity determinations with concentrations varying from 750–3000, is 0.0132. The value of  $\mu_{\text{H}}$  calculated from the sodium salt is 363. The conclusion is drawn that in bile the  $\text{CH-OH}$  group is not in the  $\alpha$ -position with respect to the carboxyl group.

**Formation of isoSerine from  $\alpha\beta$ -Dibromopropionic Acid.** CARL NEUBERG and ERICH ASCHER (*Biochem. Zeitsch.*, 1906, 1, 559–562).—In the preparation of  $\alpha\beta$ -diaminopropionic acid from  $\alpha\beta$ -dibromopropionic acid, a secondary reaction takes place in the formation of about 10% of isoserine,  $\text{NH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ . This reaction is analogous to the formation of methylisoserine from  $\alpha\beta$ -dibromobutyric acid, described by Neuberg and Kellner (1906, i, 805).

### Formation of Amines from Halogen Imino-Ethers.

KUWABARA and MORIOKI MATSUI (*Mem. Coll. Sci. Eng. Kyoto, Japan*, 1917, 1, 57—194. Compare Stieglitz, *Abstr.*, 1903, i, 235; 1904, i, 235. Stieglitz (*loc. cit.*) has shown that such compounds as chloro- and bromo-acetamino-ethyl ethers,  $C_2H_5 \cdot C(OEt) \cdot NX$ , do not undergo Beckmann rearrangement, but yield with hydrochloric acid, ethyl acetate and the corresponding halogen hypo-acid. The authors now show, however, that bromo-acetamino-, propamino-, and benzamino-ethyl ethers, reacting gently with potassium hydroxide and subsequently diluting with acid considerable amounts of the corresponding amines. As Stieglitz has shown that these esters probably have the *anti* configuration, it is suggested that on saponification the potassium salts of imino acids form are obtained, which change to the more stable *syn* isomer, undergo the Beckmann transformation, and then decompose under the influence of alkali, yielding amines as follows:

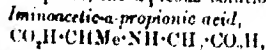


*Acetamino-ethyl ether*,  $CH_3 \cdot C(OEt) \cdot NBr$ , was obtained as an oily liquid by the action of potassium hypobromite on acetamino-ethyl ether. Its decomposition referred to above with concentrated alkali, except upon heating with water or hydrochloric acid, ethyl acetate and benzene distilling over. The corresponding *propionimino-ether* is obtained by an analogous method, and behaves like the acetate. *Benzamino-ethyl ether*,  $C_6H_5 \cdot C(OEt) \cdot NBr$ , already described by Stieglitz (*loc. cit.*), decomposes when in contact with water for some time, benzene crystallising out, and bromine and ethyl benzoate are evolved.

G. S.

**Iminoacetic or propionic Acid.** GEORGE STADNIKOFF (*Ber.*, 1907, 40, 1433—1435. Compare this vol., i, 393).—With the view of correcting the explanation previously given regarding the mode of formation of aminonitriles, the author has studied the synthesis of iminoacetic or propionic acids with the idea that these can be formed by reaction of an oxynitrile on an aminonitrile or an ester of an amino-

A concentrated aqueous solution of potassium cyanide was gradually added to a mixture of an aqueous solution of ethyl glycine hydrochloride and acetaldehyde. The mixture was subsequently saponified with caustic acid, evaporated, and the salt of the imino acid dissolved in alcohol. After successive treatment with lead hydroxide and hydrogen sulphide, the aqueous solution of the imino acid was concentrated.



crystallises from aqueous alcohol in large crystals, m. p. 222—223°. The potassium salt was prepared. Its *ethyl* ester is a colourless, viscous liquid, b. p. 122.5/12 mm., and  $D_4^{20}$  1.0457; the ester forms a crystalline derivative,  $C_{10}H_{16}O_4N_2$ , with b. p. 168—169°/13 mm., and  $d_4^{20}$  1.074.

A. McK.



**Imino- $\alpha$ -propionibutyric Acid.** GEORGE STADNER (Ber., 1907, 40, 4353—4356. Compare preceding abstract).—The inactive compounds of the formula  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$  are theoretically possible. The author has prepared these inactive acids, one of which is formed in greater amount than the other; acids can be separated by means of absolute alcohol.

By the interaction of acetaldehyde, potassium cyanide, and ethyl butyronitrile hydrochloride (or ethyl  $\alpha$ -aminobutyrate hydrochloride) the mixture of acids is obtained. The one, imino- $\alpha$ -propionibutyric acid, which is the more sparingly soluble of the two, crystallizes in needles, m. p.  $222-223^\circ$  (decomp.); its isomer was prepared. The isomeric acid could not be obtained crystalline, was converted into its copper and nickel salts and its ethyl ester,  $\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}$ , having b. p.  $126/16$  mm., and  $D_4^{20}$  1.0063. A. M. L.

**Aminocampholic Acids.** HANS RUPP and J. S. LEONARDI (Ber., 1907, 40, 4311—4318).—The compound obtained by Tafel and Leonardi (Abstr., 1897, i, 86) by heating the hydrochloride of the so-called  $\beta$ -aminocampholic acid (which really belongs to  $\alpha$ -aminocampholic acid, identical with Tafel and Eckstein's  $\alpha$ -camphidone (Abstr., 1907, 43). The authors find that the hydrochloride of  $\alpha$ -aminocampholic acid has m. p.  $247-248^\circ$ , and is insoluble in light petroleum, and Leonardi, m. p.  $268-270^\circ$ , soluble in light petroleum. The *platimichloride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{H}_2\text{PtCl}_6$ , separates in reddish-yellow leaflets.

$\beta$ -Camphoramidic acid, prepared from camphorimide and sodium hydroxide, contains the  $\alpha$ -isomeride. A separation is effected by treating the alkaline solution of the sodium salts with hydrochloric acid; so long as the solution does not contain free camphoric or  $\beta$ -camphoramidic acid alone separates. By treatment with hydrochloric acid, followed by the addition of the product to light petroleum, it forms camphoro- $\beta$ -mononitrile, which is converted by sodium in dilute alcoholic solution to  $\beta$ -aminocampholic acid. The hydrochloride has m. p.  $215-220^\circ$  and yields  $\beta$ -campholide above its m. p. or by treating its aqueous solution with solid sodium carbonate. The carbamide,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , also gives  $\beta$ -camphidone above its m. p.,  $203-204^\circ$ . By careful treatment with sodium nitrite in the cold, the hydrochloride of  $\beta$ -aminocampholic acid yields a yellow oil, which is converted by boiling barium oxide into the easily soluble barium salt,  $(\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_{11})_2\text{Ba}$ , which on acidification yields a lactone, b. p.  $121-122/12$  mm., which is probably  $\beta$ -campholide.

**Preparation of Acetamide by the Action of Ammonium Hydroxide on Ethyl Acetate.** ISAAC K. PHELPS and M. A. FARR (Amer. J. Sci., 1907, [iv], 24, 429—432).—In a previous paper (Phelps and Deming, this vol., i, 832), it has been shown that under certain conditions, a quantitative yield of formamide can be obtained from ethyl formate and ammonium hydroxide.

It is now shown that nearly theoretical quantities of acetamide can be obtained by leaving mixtures of ethyl acetate and ammonium

for about a fortnight. The reaction takes place more rapidly if a large excess of solution of ammonia is used, or if dry ammonia is passed into the mixture at  $-8^{\circ}$  to  $-10^{\circ}$  until it is saturated.  
E. G.

**Preparation of  $\alpha$ -Bromoisovalerylcarbamide.** KNOLL & CO. (D.R.P. 145962).— $\alpha$ -Bromoisovalerylcarbamide, leadets, m. p.  $149^{\circ}$ , is prepared by the action of  $\alpha$ -bromoisovaleryl bromide or chloride on dry isocyanic carbamide at  $70^{\circ}$ , is a trustworthy hypnotic, which is quite free from the unpleasant secondary effects attending the therapeutic use of valeric and  $\alpha$ -bromoisovaleric acids and their derivatives.  
G. T. M.

**Preparation of Aliphatic Thiocyanates, Nitriles, and Nitro-compounds.** PAUL WALDEN (*Ber.*, 1907, 40, 4301. Compare this 1907).—A correction. The interaction of methyl sulphate with potassium cyanide, potassium nitrite, and potassium thiocyanate has been studied by Kauffner and Pomeranz (*Abstr.*, 1901, i, 634).  
E. F. A.

**Thiocyanatotetra-amminechromium Salts.** PAUL PREIFFER and THOMER (*Zeitsch. anorg. Chem.*, 1907, 55, 361—370. Compare this 1907, 56, 694).—Complex salts of the type  $[(\text{SCN})_4\text{Cr}(\text{NH}_3)_4]\text{X}$ , in which X represents Cl, Br, SCN,  $\text{NO}_3$ ,  $\text{HSO}_4$ , have been prepared. The potassium salt is obtained by warming an aqueous solution of chlorotetra-amminechromium chloride,  $[(\text{OH})_2\text{ClCr}(\text{NH}_3)_4]\text{Cl}$ , with potassium thiocyanate; by the addition of hydrochloric or sulphuric acid to the solution of this salt, the corresponding chloride and bromide are obtained. The nitrate is prepared from the chloride by precipitation with nitric acid, and the sulphate by rubbing the chloride with sulphuric acid.

The salts in question occur in small, brick-red to orange-red crystals, soluble in water with neutral reaction. The saturated solution of the chloride contains 2% of the salt.

On warming the chloride with ethylenediamine and then treating the resulting product in aqueous solution with potassium iodide, potassiumtetra-amminechromium iodide,  $[\text{Cr}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]\text{I}_2 \cdot \text{H}_2\text{O}$ , was obtained in yellow crystals.

Attempts to prepare compounds containing  $\text{Cl}_2$  or  $\text{Br}_2$  instead of  $\text{SCN}_4$  in the nucleus have so far been unsuccessful.  
G. S.

**Preparation of Dialkylbromoacetamides from Dialkylcyanoacetic Acids.** PAUL HOERING (D.R.P. 186739. Compare *Abstr.*, 1907, 40, 1045).—The dialkylbromoacetamides, which are valuable drugs, are readily obtained from the dialkylcyanoacetic acids by first converting these into dialkylacetoneitriles, bromodialkylacetoneitriles, and then by hydrolysis into the required amide. Diethylcyanoacetic acid when repeatedly distilled at  $145$ — $200^{\circ}$ , or on heated under pressure, is converted into diethylacetoneitrile (diethylacetoneitrile),  $\text{CH}_3\text{Et}_2\text{CN}$ , b. p.  $144^{\circ}$ ; diisopropylacetoneitrile (diisopropylacetoneitrile),  $\text{CH}(\text{Pr})_2\text{CN}$ , b. p.  $183$ — $184^{\circ}$ , is a colourless liquid with an agreeable odour.

(On bromination, the two preceding compounds yield respectively *bromolithylacetoneitrile*, colourless oil, b. p. 183—186°, and *bromodipropylacetoneitrile*, b. p. 209—211°.

*Bromolithylacetamide*,  $\text{CHEt}_2\cdot\text{CONH}_2$ , m. p. 64—65°, is prepared by hydrolysing the corresponding acetonitrile with concentrated sulphuric acid on the water-bath. G. T. W.

**Action of Diazo-derivatives of Aliphatic Compounds: Cyanogen and its Derivatives. IV. and V. Hydrocyanic Acid.** ALBERTO PERATONER and F. CARLO PALAZZANI. *Accad. Lincei*, 1907, [v], 18, ii, 432—441, 501—513. (Chem. Abstr. vol. i, 579).—According to von Pechmann (Abstr., 1895, i, 324), the action of diazomethane on hydrocyanic acid yields cyanogen. The authors, who have studied the interaction of these compounds in the gaseous state and in ethereal solution, and also the action of gaseous diazomethane on liquid hydrogen cyanide, find that cyanogen is only a secondary product of the reaction, and is always accompanied by methylearhylamine; no trace of a triazole derivative is found. The previous results indicate that, with a hydrogen cyanide of this structure, the synthesis of osotriazole should take place with great readiness.

The literature dealing with the structure and tautomerism of hydrocyanic acid is discussed. I. H. P.

**The Study of Hydro-aromatic Substances.** EDWARD LEITCH ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, JR., MARTIN O. FRIEDMAN, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1906, 76, 267).—A résumé of recent work on hydroaromatic substances, containing references to a comparative study of dihydrolaurelene, dihydrolaurelene, and 1:1-dimethylcyclohexane, and to the action of phosphorus pentachloride on trimethyldihydroresorcin. G. T. W.

**Reduction of Trimethylene [*cycloPropane*].** RICHARD G. STATTEN and JAMES BRUCE (*Ber.*, 1907, 40, 4456—4458).—Trimethylene is reduced by hydrogen and nickel at 30—45°, cyclopropane reduced to butane only at 180° (following abstract). It is now found that cyclopropane, which in its constitution lies between cyclobutane and cyclobutane, is reduced to propane at an intermediate temperature, the reduction commencing at 80° and taking place rapidly at 100°. Contrary to Wolkoff and Menshutkin's statement (*Mém. chim.*, i, 196, 321; 1900, i, 423), pure cyclopropane is readily obtained by the action of zinc dust on trimethylene dibromide (Gustavson, *Ber.*, 1899, i, 421). G. T. W.

**Derivatives of *cycloButane*. II.** RICHARD WILSON and JAMES BRUCE (*Ber.*, 1907, 40, 3979—3999).—*cycloButane* is prepared by distillation of trimethylcyclobutylammonium hydroxide, b. p. 100—102°, of  $\Delta^2$ -butadiene. As was shown previously (Wilson and Schmiedel, *Abstr.*, 1905, i, 514), these hydrocarbons yield *trans*- $\Delta^2$ -butadiene which can be separated by treatment with dimethylamine, and *trans*- $\Delta^2$ -butadiene dibromide is converted into *trans*-tetramethylammonium

pure *cyclobutene* dibromide remaining unchanged. Pure *cyclobutene* is now obtained by reduction of its dibromide with zinc and alcohol; on reduction by means of finely-divided nickel and hydrogen (Sabatier and Senderens, Abstr., 1905, i, 333, 401) at 100°, *cyclobutane* is formed, whilst, when reduced at 180–200°, it forms *cyclobutadiene*. Attempts to prepare *cyclobutene* by distillation of aminocyclobutane phosphate (Harries, Abstr., 1901, i, 134) led to the formation of butadiene. The preparation of *cyclobutane* completes the cyclopropane-cyclononane; a table is given showing the rise of  $d_4^{20}$ ,  $d_4^{25}$ ,  $d_4^{30}$ ,  $D_4^0$ , and mol. vol. at 0° throughout the series. The weight of two neighbouring members of the series differ on the average by 13, except in the case of the last pair, the mol. vol. of *cyclooctane* exceeding that of *cyclooctane* by 28.54. The molecular weights of all members of the series to *cyclooctane*, so far as calculated, agree with those calculated, whereas that observed for *cyclooctane* (Zelinsky, this vol., i, 780) exceeds the calculated by 0.75. *Cyclobutene*, b. p. 1.5–2°, 729 mm.,  $D_4^{20}$  0.733, has a slight odour, is readily soluble in acetone, is absorbed by caoutchouc, reduces potassium permanganate instantaneously, and forms additive compounds with chlorine and bromine, but slowly with iodine.

*Cyclobutamine phosphate*,  $C_4H_7NH_2H_2PO_4$ , crystallises in prisms, m. p. 147°. The action of bromine on the product obtained on heating the phosphate leads to the formation of the two stereoisomeric *cyclobutene* tetrabromides, m. p. 118° and 40–41° (Clamianci, Abstr., 1886, 521), or of butadiene dibromide.

*Cyclobutane*,  $C_4H_8$ , b. p. 11–12°, 760 mm. (corr.), remains liquid at -119°,  $D_4^{20}$  0.718,  $n_D^{20}$  1.37520, has a slight odour, burns with a luminous flame, and is stable towards concentrated hydriodic acid and bromine in chloroform solution at the ordinary temperature. It is formed by reduction of *cyclobutene*, *cyclobutane*, or  $\phi$ -butyl bromide with hydrogen and nickel at 180–200°, has b. p. -4° to -1.2 mm.

*Cyclobutene dichloride*,  $C_4H_6Cl_2$ , is a colourless liquid, b. p. 13.5–14.5°, 760 mm. (corr.),  $D_4^{20}$  1.235,  $D_4^{25}$  1.213, and is not inflammable; it imparts a green colour to a bunsen flame. *Cyclobutene* dichloride crystallises in plates, m. p. 48°,  $D_4^{20}$  2.659, has an odour of sulphur, and commences to dissociate at 140°.

The tendency of the *cyclobutene* derivatives to yield acyclic compounds, especially in reactions at high temperatures, is well known. It has been shown that *cyclobutene* dibromide and dichloride do not react with bromine alone even when heated, but, with bromine in presence of iron, *cyclobutene* dibromide yields *ααββ* (or *ααββ*) *tetrabromobutane*, which is obtained as a colourless oil, b. p. 138–145°,  $D_4^{20}$  2.562,  $D_4^{25}$  2.529,  $n_D^{20}$  1.60771, and on further bromination in presence of iron loses hydrogen bromide, forming an oily product containing small amounts of hexabromocyclobutane, and when heated with alcoholic potassium hydroxide yields a product,  $C_4H_6Br_2$ , b. p. 13–14 mm.,  $D_4^{20}$  1.99. This is readily oxidised by potassium permanganate, forms an additive compound with 1 mol. of bromine, and is probably a *cyclopropane* derivative.

The action of bromine on *cyclobutene* dichloride in presence of

iron leads to the formation of *disubstituted bromobutane*, b. p. 133—135 mm.,  $D_4^{20}$  2.1, *disubstituted bromobutane*, b. p. 155—157 mm.,  $D_4^{20}$  2.47, which is the chief product, and *disubstituted bromobutane*, b. p. 176—185/21 mm.,  $D_4^{20}$  2.69.

Whilst *cyclobutene dibromide* does not react with bromine in the presence of iodine, *cyclobutene di-iodide* reacts with bromine, yielding tetrabromobutane.

*a. Bromobutadiene*,  $\text{CHBr:CH:CH:CH}_2$ , formed together with a small amount of hydrocarbon, which gives a white precipitate with silver nitrate by the action of potassium hydroxide on  $\alpha$ -butadiene dibromide, is obtained as a mobile liquid, b. p. 92—94/760 mm.,  $D_4^{20}$  1.416, has an odour of vinyl bromide, and gradually changes into a sparingly soluble, dark brown mass, probably a polymerisation product. *a. Bromobutadiene* combines slowly with 2 mola. of bromine forming *1,3,4,5-tetrabromobutane*,  $\text{C}_4\text{H}_2\text{Br}_4$ , which is a colourless solid, m. p. 165—170/10 mm.,  $D_4^{20}$  2.78, and consists of a mixture of two crystalline isomerides, which form prisms, m. p. 108, and plates, m. p. 57—58°, respectively.

*1:1-Dibromocyclobutane*,  $\text{C}_4\text{H}_2\text{Br}_2$ , b. p. 157—158/5 mm.,  $D_4^{20}$  (corr.) 1.960,  $D_4^{20}$  1.933,  $n_D^{20}$  1.53618 (Kijner, Abstr., 1907, i, 355), is prepared by the action of hydrogen bromide on *1:1:1-tribromocyclobutene* in glacial acetic acid solution. *1:1:1-Tribromocyclobutane*,  $\text{C}_4\text{H}_2\text{Br}_3$ , formed by the action of bromine on *1:1:1-tribromocyclobutene* in chloroform solution, is a colourless oil, b. p. 19—20 mm.,  $D_4^{20}$  2.374, has an odour of camphor, is soluble in a current of steam, and when treated with methylalcoholic potassium

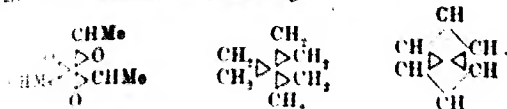
hydroxide yields *1:2-dibromo- $\Delta^1$ -cyclobutene*,  $\text{CHBr:CH:CH}_2\text{CH}_2$ , which is obtained as an oil, b. p. 155—156°,  $D_4^{20}$  2.036, has an odour of vinyl bromide, gradually polymerises, and on oxidation with potassium in neutral solution yields succinic acid.

*1:1:2:2-Tetrabromocyclobutane*,  $\text{C}_4\text{H}_2\text{Br}_4$ , formed by the action of bromine on *1:2-dibromo- $\Delta^1$ -cyclobutene* in chloroform solution, crystallises in hexagonal plates, m. p. 126°, distils unchanged in a vacuum, and yields *1:2-dibromo- $\Delta^1$ -cyclobutene* when heated with concentrated alcoholic potassium hydroxide. A mixture of this tetrabromocyclobutane with the somewhat similar  $\alpha$ -butadiene tetrabromide has a melting point about 50°.

*1:1:2:2:3-Pentabromocyclobutane*,  $\text{C}_4\text{H}_2\text{Br}_5$ , formed by the action of bromine and iron powder on tetrabromocyclobutane, is a colourless oil, b. p. 175—185/19 mm.,  $D_4^{20}$  2.88, has a terpene odour, and on treatment with bromine and iron powder at 50° yields *1:1:2:2:3:4-Hexabromocyclobutane*,  $\text{C}_4\text{H}_2\text{Br}_6$ , which crystallises from benzene in plates, m. p. 186.5° (corr.), and decomposes on treatment with bromine, when heated in a tube. This hexabromocompound resembles Sabaneff's hexabromotetramethylene, m. p. 184° (corr.) (Noyes and Tucker, Abstr., 1897, i, 261).

**Improbability of Kekulé's Hypothesis.** RAYMOND V. MAYER (Chem. Zentr., 1907, i, 1787; from Mon. sci., 1907, vi, 21—24—244—249).—The author discusses the known objections to Kekulé's

and maintains that the formation of aromatic from aliphatic compounds, for example, paraldehyde from acetaldehyde and benzene from ethylene, is better understood by the following formulae as the following :



W. H. G.

**Cerous Salts of Certain Organic Acids.** GILBERT T. MORGAN and EDWARD CAHEN (*Pharm. J.*, 1907, 78, 428—430. Compare *ibid.* 1907, 91, 475).—*Cerous naphthalene-2:7-disulphonate*,  $\text{Ce}[\text{C}_{10}\text{H}_7(\text{SO}_3)_2]_3 \cdot 25\text{H}_2\text{O}$ ,

obtained in small, nacreous leaflets having a pink colour; the pink crystallisation is only removed completely at  $160^\circ$ . *Cerous naphthalene-2 sulphonate*,  $\text{Ce}[\text{C}_{10}\text{H}_7\text{Me}(\text{NO}_2)\text{SO}_3]_3 \cdot 10\text{H}_2\text{O}$ , crystallises in plates and intumesces on heating, leaving a bulky residue of cerous oxide. *Cerous isovalerate*,  $\text{Ce}_3(\text{C}_5\text{H}_9\text{O}_2)_6 \cdot 5\text{H}_2\text{O}$ ; *benzoate*,  $\text{Ce}_2(\text{C}_6\text{H}_5\text{O}_2)_4 \cdot 5\text{H}_2\text{O}$ ; *cinnamate*,  $\text{Ce}_2(\text{C}_9\text{H}_7\text{O}_2)_4 \cdot 5\text{H}_2\text{O}$ ;

*coumarate*,  $\text{Ce}_2(\text{C}_{10}\text{H}_7\text{O}_4)_4 \cdot 9\text{H}_2\text{O}$ , are white, amorphous or microcrystalline powders, very sparingly soluble in water. *Cerous salicylate*,  $\text{Ce}_2(\text{C}_7\text{H}_5\text{O}_3)_4 \cdot 5\text{H}_2\text{O}$ , is soluble in water, and crystallises from a hot solution in groups of small, light needles having a pale mauve colour.

*Cerous lactate* is very soluble; when its aqueous solution is heated over sulphuric acid, it solidifies to a crystalline mass, the composition of which corresponds with a salt containing  $7\text{H}_2\text{O}$ . *Cerous oleate* is prepared by stirring precipitated cerous hydroxide and oleic acid together in a buff-coloured substance having the consistence of lard.

H. M. D.

**Preparation of Aromatic Fluoro-compounds by Decomposition of Diazo- and Bisdiazo-compounds with Concentrated Hydrofluoric Acid.** VALENTINER and SCHWARZ (D.R.-P. 1866005). The methods for obtaining fluoro-derivatives of the aromatic hydrocarbons have hitherto only furnished small yields of the products. The authors found that the diazo-fluoride produced by adding hydrofluoric acid to a solution of the diazo- or bisdiazochloride is readily decomposed catalytically by ferric chloride, yielding the aromatic fluoro-derivative. 1:4-Difluorodiphenyl is produced on adding successively concentrated hydrofluoric acid and 10% ferric chloride solution to a solution of bisdiazodiphenyl chloride. The fluoro-derivatives of benzene, toluene, and naphthalene may be obtained similarly.

G. T. M.

**Derivatives of Diphenyliodonium Hydroxide: New Series of Heterocyclic Compounds containing Iodine in the Main Chain.** LUIGI MASCARELLI (*Atti R. Accad. Lincei.*, 1907, 16, ii, 562—567).—By treating di-iodoxydiphenyl or di-iododiphenyl with moist silver oxide (compare Hartmann and Voss, *Ann.*, 1894, 1, 242), the author has obtained diphenylene-

iodonium hydroxide,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{I} \cdot \text{OH}$ , closure of the ring being effected by the iodine atom becoming trivalent.

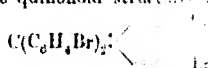
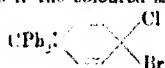
*o*-*Di-iododiphenyl*,  $\text{C}_6\text{H}_4\text{I} \cdot \text{C}_6\text{H}_4\text{I}$ , prepared by diazotising *o*-diphenyl and decomposing the diazo-compound with potassium, separates from water as a pale yellow, microcrystalline powder, m. p. 210—211°. Its *tetrachloride*,  $\text{C}_6\text{H}_4(\text{Cl}_2\text{I} \cdot \text{C}_6\text{H}_4\text{Cl}_2\text{I})$ , separates from chloroform in yellow, acicular crystals, m. p. 130—135° (decomp.).

*o*-*Di-iodoxydiphenyl*,  $\text{OI} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{OI}$ , obtained by the action of dilute potassium hydroxide solution on *o*-di-iododiphenyl tetrachloride, is a yellow, amorphous powder, m. p. 109—110°.

*o*-*Di-iodoxydiphenyl*,  $\text{IO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$ , obtained on heating *o*-di-iodoxydiphenyl with water, forms slender, white crystals, m. p. 145—148° (decomp.).

Diphenyleneiodonium hydroxide, crystallising in slender, white filaments, m. p. 145—148° (decomp.), was not analysed. Its *acetyl* derivative,  $\text{I}(\text{C}_6\text{H}_4)_2\text{Ac}$ , crystallises in hard, white prisms, m. p. 191—192° (decomp.), and has the normal molecular weight in *fructose* urethane. The *oxalate*,  $\text{C}_2\text{O}_4[\text{I}(\text{C}_6\text{H}_4)_2]_2$ , crystallises from acetic acid in colourless prisms, m. p. 191—192°.

**Problem of the Structural Formula of "Triphenylmethane."** ALEXEI E. TSCHITSCHIRABIN (*Ber.*, 1907, 40, 3965—3970). The author criticises Gomberg's quinonoid theory of the coloured salts derived from triphenylcarbinol (this vol., i, 504) from the point of view as does Baeyer (this vol., i, 691). When treated with water the strongly coloured double salts of stannic chloride and *o*- and *p*-bromo triphenylmethyl chlorides yield hydrogen chloride and not even traces of hydrogen bromide. In the same manner salts of alkali bromide is obtained together with the alkali chloride and *p*-bromo- and *o*-*p*-bromo triphenylmethyl chlorides are heated with sulphur dioxide at 50° and subsequently with an aqueous solution, whereas if the coloured salts had the quinonoid structure the



the isomerisation would lead to the formation of mixtures of acids, chlorides and bromides and hence of alkali chlorides and bromides.

Schmidlin's supposed isomeric magnesium triphenylmethyl chlorides (this vol., i, 26) are criticised. Both the  $\alpha$ - and  $\beta$ -modification react with benzoyl chloride and ethyl benzoate, forming benzophenone in 80% yield. Contrary to Schmidlin's statement, the  $\alpha$ -modification on treatment with carbon dioxide in ethereal solution yields triphenylacetic acid in a 90% yield; the action of water on the  $\beta$ -modification leads to the formation of triphenylmethane in 90% yield. The *p*-benzoyltriphenylmethane obtained by Schmidlin is formed probably by condensation of triphenylmethane with benzaldehyde.

**Phenanthrene Series. XXI. Hydrophenanthrenes.** SCHMIDT and ROBERT MEZGER (*Ber.*, 1907, 40, 4240—4257). The hydrophenanthrenes have been referred to previously.

phenanthrene (Bamberger and Ledter, *Abstr.*, 1888, 292) and tetrahydrophenanthrene (Graebe, *Abstr.*, 1873, 894). By using different methods and conditions of reduction, the authors have succeeded in preparing a number of hydrogenated derivatives coming between the limiting di- and dodecahydrophenanthrenes. The lower members of this series are obtained by means of sodium and alcohol, and the higher ones by means of phosphorus and acetic acid. In order to obtain pure products and not mixtures of hydrogenated derivatives difficult to resolve into their constituents, it is necessary to adhere closely to the conditions laid down by the authors. The experiments of Liebermann and Spiegel (*Abstr.*, 1889, 123) have been repeated, the results indicating that the perhydrophenanthrene described by these authors does not exist.

**Di-hydrophenanthrene**,  $C_{14}H_{12}$ , prepared either by the action of sodium and amyl alcohol on phenanthrene or by passing a mixture of hydrogen and phenanthrene vapour over reduced nickel at  $200^{\circ}$ , separates from alcohol in shining, snow-white leaflets, m. p.  $94-95^{\circ}$ , b. p.  $314-317.39$  mm., and closely resembles phenanthrene in its solubility and other properties. It is not acted on by bromine, but forms a picrate,  $C_{14}H_{10}C_6H_3O_7N_3$ , forming brick-red needles, m. p.  $107-108^{\circ}$ . On oxidation, it yields phenanthraquinone in almost equal proportion.

**Tetrahydrophenanthrene** (2:7:9:10- or 4:5:9:10-tetrahydrophenanthrene),  $C_{14}H_{14}$  (compare Graebe, *loc. cit.* and Bamberger, *loc. cit.*), a colourless oil, b. p.  $307-317.737$  mm., m. p.  $-4^{\circ}$  to  $-5^{\circ}$ ,  $D_4^{20}$  1.082,  $n_D^{20}$  1.5820. It gives a picrate,  $C_{14}H_{12}C_6H_3O_7N_3$ , forming brick-red needles, m. p.  $105-106^{\circ}$ .

**Tri-hydrophenanthrene** (2:7:9:10- or 4:5:9:10-tetrahydrophenanthrene),  $C_{14}H_{14}$ , is a yellow oil, b. p.  $302-305-737$  mm., m. p.  $-3$  to  $-4^{\circ}$ ,  $D_4^{20}$  1.085,  $n_D^{20}$  1.5820, more stable to the action of air than the  $\alpha$  derivative, and yields no picrate.

**Tri-hydrophenanthrene**,  $C_{14}H_{16}$ , is a colourless oil, b. p.  $302-305-737$  mm., m. p.  $-7^{\circ}$  to  $-8^{\circ}$ ,  $D_4^{20}$  1.045,  $n_D^{20}$  1.5704, and yields no picrate.

**Tri-hydrophenanthrene** (compare Graebe, *loc. cit.*),  $C_{14}H_{16}$ , is a colourless oil, b. p.  $282-737$  mm., m. p.  $-11^{\circ}$  to  $-12^{\circ}$ ,  $D_4^{20}$  1.012,  $n_D^{20}$  1.5335; it does not form a picrate.

**Tri-hydrophenanthrene**,  $C_{14}H_{16}$ , is a colourless oil, b. p.  $275-737$  mm., m. p.  $-18^{\circ}$  to  $-20^{\circ}$ ,  $D_4^{20}$  0.993,  $n_D^{20}$  1.5335; it does not yield a picrate.

**Dodecahydrophenanthrene**,  $C_{14}H_{22}$ , is obtained as a colourless oil, b. p.  $269-737$  mm.,  $D_4^{20}$  0.964,  $n_D^{20}$  1.5119, remaining liquid at  $-100^{\circ}$ ; it gives no picrate.

No more highly hydrogenated derivative than the dodecahydrophenanthrene could be prepared.

T. H. P.

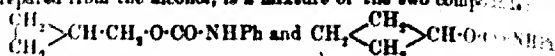
**Isomerisation of Cyclic Amines containing the Side-chain**  
 (NH). The Nature of the Alcohol obtained from the

Amine  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{NH}_2$ . NICOLAUS J. DEMJANOFF (*Ber.*, 1907, 40, 437-439; *J. Russ. Phys. Chem. Soc.*, 1907, 39, 1077-1085).—The



amine and its corresponding alcohol were prepared previously (*ibid.*, 1906, 37, 622), some modifications being made in the formation of the nitrile,  $\text{CH}_2 > \text{CH} \cdot \text{CN}$ . The phenyl urethane

prepared from the alcohol, is a mixture of the two compounds:



When oxidised with chromic acid, the alcohol yields a mixture of aldehydes, which form two semicarbazones, one of which,



m. p. 125–126°, is soluble in ether, the other has m. p. 215°, and is insoluble in ether, and is identical with the one obtained from the

alcohol prepared from aminocyclobutane,  $\text{CH}_2 < \text{CH} > \text{CH} \cdot \text{NH}_2$ , is

probably also with Kijner's semicarbazone of ketocyclobutane. The alcohol is also oxidised readily with nitric acid, forming nitroacetic acid, whilst the pure cyclopropyl carbinol yields only traces of nitroacetic acid. It is thus evident that, contrary to Dalle's statement (*ibid.* 1902, i, 525), the amine,  $\text{CH}_2 > \text{CH} \cdot \text{CH}_2 \cdot \text{NH}_2$ , when converted into an

alcohol, isomerises partially, forming a cyclobutane derivative.

**Preparation of Derivatives of Formaldehydesulphoxylic Acid containing Nitrogen.** RADISCHE ANILIN- & SOEHLICH (D.R.-P. 185689. Compare Abstr., 1906, i, 480).—A mixture of aniline, sodium formaldehydesulphoxylate, and water is heated at 70–80° until the base has dissolved. The solution when concentrated under diminished pressure yields a deposit of acicular crystals of a new compound of aniline and the sulphoxylate. This compound decomposes in the dry state, but is stable in the form of a paste. The homologues of aniline yield similar products, and a corresponding compound of ammonia may be obtained as a white, porous mass which differs from the original formaldehydesulphoxylate in being insoluble in methyl alcohol. The aliphatic amines give rise to similar compounds. These formaldehydesulphoxylate derivatives are powerful reducing agents, and may be employed in the printing of fabrics. They reduce indigo-carmin on warming, or even in the cold in the presence of mineral acids. When warmed with aqueous sodium hydroxide, these new compounds are reconverted into the generators.

**Derivatives of *m*-Iodonitrobenzene, *m*-Iodoaniline, and *m*-Iodoacetanilide containing Multivalent Iodine.** G. W. WILLGERODT and E. HJALMAR WIKANDER (*Ber.*, 1907, 40, 1600).

The following salts of di-*m*-nitrophenyliodinium hydroxide are described. The *chloride*, m. p. 214°, white needles, decompose as powder, decomposing at 183–184°; *iodide*, m. p. 130° (decoloring), yellowish-white powder; *periodide*,  $(\text{C}_6\text{H}_3\text{NO}_2)_2\text{I}_2$ , m. p. 100° (decomp.), dark brown needles, obtained from the preceding salts.

*iodoacetanilide*; *platinichloride*,  $2(C_6H_5 \cdot NO_2)_2 \cdot PtCl_2$ , m. p. 196—197°; *mercurichloride*, dark brown needles; *nitrate*, m. p. 194°, white needles; *potassium dichromate*, m. p. 168.5°; *dichromate*, yellow powder, exploding at 135°.

*m*-Nitrophenyliodinium chloride,  $NO_2 \cdot C_6H_4 \cdot IPhCl$ , m. p. 170—172°. Prepared by triturating *m*-nitrophenyl iododichloride and mercury in water; the *mercurichloride* has m. p. 152°; the *platinichloride* decomposes at 177°; the *iodide* at 133°, and the *periodide*,  $S_2O_8H_2 \cdot IPhI_2$ , has m. p. 118° (decomp.).

*m*-Nitroiodoxy-, and iodonium compounds have not yet been prepared from iodoanilines.

*m*-Acetylaminophenyl iododichloride,  $NHAc \cdot C_6H_4 \cdot ICl_2$ , is obtained in small crystals by passing chlorine into a solution of *m*-iodoacetanilide in glacial acetic acid at 0°, but not in chloroform; it decomposes at 114°. Its treatment with a solution of sodium carbonate is converted into *m*-iodoacetanilide, which decomposes at 72°. C. S.

**Derivatives of *p*-Iodoacetanilide containing Multivalent Iodine and *p*-Aminodiphenyliodonium Compounds.** CONRAD LUDWIG and WALTER NAGELI (*Ber.*, 1907, 40, 4070—4077, compare preceding abstract).—*p*-Acetylaminophenyl iododichloride,  $NHAc \cdot C_6H_4 \cdot ICl_2$ , m. p. 110° (decomp.), prepared in the usual manner, forms very stable yellow needles. Cold sodium carbonate solution converts it into *p*-iodoacetanilide, which decomposes at 114°, and fuses with potassium dichromate to a yellow basic chromate,



which decomposes at 85—90°. *p*-Iodoxyacetanilide,  $NHAc \cdot C_6H_4 \cdot IO_2$ , prepared from the iodo compound and a small excess of sodium carbonate solution, the reaction being accelerated by the addition of a few drops of glacial acetic acid, explodes at 163°.

*p*-Acetylaminodiphenyliodonium hydroxide,  $NHAc \cdot C_6H_4 \cdot IPh \cdot OH$ , is obtained in aqueous solution from iodoxybenzene and *p*-iodoacetanilide in the usual manner, or by decomposing the iodonium iodide with moist silver oxide. The *chloride*, m. p. 190°, is prepared from the hydroxide, or from mercury diphenyl and *p*-acetylaminodiphenyliododichloride. The *bromide* has m. p. 183°; the *iodide*, m. p. 145°; the *periodide*, m. p. 145° (decomp.); *nitrate*, m. p. 180.5°; *dichromate*, decomp. 60°; *platinichloride*, m. p. 166°; *mercurichloride*, decomp. 100°.

*p*-Acetylaminodiphenyliodonium hydroxide,  $(NHAc \cdot C_6H_4)_2 \cdot I \cdot OH$ , forms colorless salts. The *chloride* is too soluble to be isolated in the crystalline state. The *bromide*, m. p. 165°; the *iodide*, m. p. 176.5°; *dichromate*, m. p. 176° (decomp.); *platinichloride*, m. p. 162° (decomp.); *mercurichloride*, m. p. 162°. *p*-Acetylaminophenyl-*p*-tolyliodonium iodide forms the salts: *chloride*, m. p. 204.5°; *bromide*, m. p. 185°; *iodide*, m. p. 151°; *dichromate*, m. p. 140° (decomp.); *platinichloride*, decomp. at 159°, and then has m. p. 178°; *mercurichloride*, m. p. 145°.

Hydrolysis of *p*-acetylaminodiphenyliodonium chloride takes place when the substance is heated with 10% alcoholic hydrogen chloride

for one hour on the water-bath, the products being ethyl acetate and the hydrochloride of *p*-aminodiphenyliodinium chloride,  
 $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{I}\cdot\text{PhCl}\cdot\text{HCl}$ .

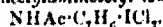
The corresponding *platinichloride*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{I}\cdot\text{Ph}\cdot\text{HPtCl}_2$ , prepared from a strongly acidified solution of the iodinium chloride and excess of platinum chloride, crystallises in small needles, m. p. 134° (decomp.).

The *platinichloride*,  $2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{I}\cdot\text{Ph}\cdot\text{PtCl}_2$ , is a yellow, crystalline precipitate obtained by adding platinum chloride to an aqueous solution of the iodinium chloride, and decomposes above 210°. The *bromide* has m. p. 182.5°; the *iodide*, m. p. 164°; the *dichromate*, m. p. 139°, and has m. p. 143° (decomp.).

Azo-compounds are obtained in an impure state from a benzene solution of *p*-aminodiphenyliodinium bromide and  $\beta$ -naphthylamine *H* salt.

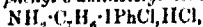
**Derivatives of *p*-Iododiphenyliodinium Chloride and *p*-Iodoaceto-*o*-toluidide containing Multivalent Iodine.** Preparation of Chloroacetylamines containing Iodine. — WILDERODT and KARL HEUSNER (*Ber.*, 1907, 40, 457) have prepared Meyer and Hartmann's *p*-iododiphenyliodinium iodide salt is prepared by treating the diazotised solution of the hydrochloride of *p*-aminodiphenyliodinium chloride (preceding abstract) with a solution of potassium iodide (2 mols.); it has m. p. 145°; the *bromide* has m. p. 166°.

*Iodoaceto-*o*-toluidide*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{I}$ , m. p. 169.5°, is obtained from *neo*-*o*-toluidide and iodine monochloride in glacial acetic acid; the position of the halogen is not yet determined, but it is probably near to the acetyl-amino-group. The following compounds are prepared by the usual methods: *o*-acetylaminotolyl iododichloride,



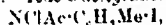
forms stable yellow crystals and decomposes at 109°; the *iodoxy*-compound is very unstable, and the *iodoxy*-compound has not been isolated. *Phenyl-*o*-acetylaminotolylidinium hydroxide* forms a chloride, m. p. 179°; *bromide*, m. p. 173.5°; *iodide*, m. p. 152°; *dichromate*, decomposes at 65°; *platinichloride*, beginning to decompose at 100°, and melting (decomp.).

The *hydrochloride of phenyl-*o*-aminotolyl iodinium chloride*,



is obtained by hydrolysing the preceding iodinium chloride by alcoholic hydrogen chloride; it begins to decompose at 130°, and has m. p. 255° (decomp.). The *bromide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{I}\cdot\text{PhBr}$ , has m. p. 175°; the *iodide*, m. p. 169°; *dichromate*, decomp. 155°; *platinichloride*, m. p. 157° (decomp., beginning at 120°).

*Iodoxy-*o*-acetylchloroaminotoluene*,  $\text{NClAc}\cdot\text{C}_6\text{H}_3\cdot\text{Me}\cdot\text{IO}_2$ , is obtained from *o*-acetylaminotolyl iododichloride and sodium hypochlorite in aqueous acid solution; the composition is controlled by an estimation of the halogens and of the iodine liberated from potassium iodide. *Iodo-chloroamino-*p*-iodoxybenzene*,  $\text{NClAc}\cdot\text{C}_6\text{H}_3\cdot\text{IO}_2$ , prepared in a similar manner, explodes at 158°. *Iodo-*o*-acetylchloroaminotoluene*,



m. p. 92° (decomp., beginning at 85°), is obtained by adding sodium

of sodium hypochlorite to a not too concentrated solution of acetophenone in glacial acetic acid. *Acetylacetophenone-p-toluidine*,  $\text{NHAc}(\text{C}_6\text{H}_4)_2\text{I}$ , prepared in a similar manner, has m. p. 127° (beginning at 115°). G. S.

**The Transformation of Aromatic Nitroamines and Allied Substances and its Relation to Substitution in Benzene Derivatives.** FREDERIC R. KIPPING, KENNEDY J. P. ORTON, and ARTHUR KUHMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Report, 1906, 76, 159—161*).—A summary of the reactions of *p*-nitroaminobenzene and of changes which lead to the displacement of halogen by hydroxyl in halogenated benzene diazo-compounds. G. T. M.

**Preparation of *p*-Nitrodiphenylamine and its Derivatives.** G. T. MERRIFIELD (D.R.P. 185663).—Although *p*-chloronitrobenzene and aniline do not interact alone, a mixture of the two compounds was caused to condense by heating with potassium carbonate in presence of a small proportion of cuprous iodide. Nitrobenzene was employed as a diluent, and the aniline may be replaced by other aromatic amines. 4-Nitrophenyl-*p*-tolylamine, green crystals, m. p. 100°, was thus obtained from *p*-toluidine; 4 : 4'-dinitrodiphenylamine was produced from *p*-nitroaniline, *p*-chloronitrobenzene, potassium carbonate, and cuprous iodide when the mixture was heated for 24 hours in boiling nitrobenzene. When the *p*-nitroaniline is replaced by anthranilic acid, 4-nitrophenylanthranilic acid, m. p. 211°, is obtained. G. T. M.

**Beckmann's Rearrangement.** MITSURU KUHARA and TADAKA KUSAKI (*Mem. Coll. Sci. Eng. Kyōto, 1907, 1, 254—264*; Compare Beckmann, *Abstr.*, 1894, i, 240).—Varying quantities of benzoyl oxime, dissolved in chloroform, were heated with a constant quantity of acetyl chloride for some hours at 100—110°, and it was found that the amount of benzanilide formed by the Beckmann rearrangement was proportional to the oxime concentration only; it was suggested that the action of the acetyl chloride in the reaction is catalytic. Further, when a fixed amount of acetyldiphenyl oxime is heated for some time with varying proportions of hydrochloric acid in chloroform solution, the amount of benzanilide formed is approximately proportional to the concentration of acid. Chlorobenzeneaniline,  $\text{NPh}_2\text{CPhCl}$ , which may be an intermediate product of the Beckmann rearrangement, reacts immediately with a mixture of acetic anhydride and glacial acetic acid with formation of benzanilide and acetyl chloride.

On the basis of these results and of those of previous observers, it is suggested that the Beckmann rearrangement in the presence of acetyl chloride depends on the formation of an intermediate compound of acetyl chloride and the oxime, which undergoes rearrangement under the catalytic influence of the hydrochloric acid produced, the

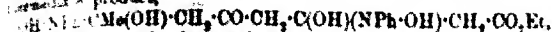
latter also taking a direct part in the final stage of the reaction, in which the substituted amide is produced and acetyl chloride is generated.

**N-Alkylketoximes.** JOHANNES SCHERER and H. BAER (Annalen, 1907, 367, 25—46. Compare Beckmann and Scherer, this vol., i, 829).—Aldehydes react with  $\beta$ -substituted hydroxylamines forming additive compounds which undergo intramolecular condensation to *N*-alkylaldoximes. It was to be expected that the products obtained from the action of  $\beta$ -substituted hydroxylamines on acetone and ethyl acetoacetate are formed in the same manner. A comparison of these substances with the *N*-alkylaldoximes leads to the conclusion that the first stage of the reaction is the formation of an additive compound; the further action, however, varies with the ketone and the  $\beta$ -substituted hydroxylamine. The condensation products of acetone and  $\beta$ -substituted hydroxylamines differ from the *N*-alkylaldoximes in that they decompose on fusion, are unstable in solution, have mol. weights double those corresponding to the formula  $\text{CRR}'\text{N} \begin{smallmatrix} \text{NR}' \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ , and are decomposed by phenylhydrazine or

acid chlorides or anhydrides. The action of hydrogen chloride on *N*-alkylacetoximes in ethereal solution leads to the formation of an unstable, white substance, probably a decomposition product. The action of hydrogen chloride on a mixture of acetone and phenylhydroxylamine leads to the formation of the hydrochloride of the transformation product of the latter. When boiled with hydrochloric acid, *N*-arylacetoximes are hydrolysed, forming their corresponding hydroxylamine being then reduced to the corresponding amine. Mesityl oxide condenses with phenylhydroxylamine, forming a solid, m. p. 107°, and with benzylhydroxylamine, forming an additive compound,  $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}$ , m. p. 101—102°. The reaction of acetone with arylhydroxylamines cannot be preceded by condensation of the acetone. When heated with hydroxylamino hydrochloride and sodium carbonate in alcoholic solution, the condensation product of acetone and phenylhydroxylamine yields a product,  $(\text{C}_6\text{H}_5)_2\text{ON}$ , m. p. 112°. Similarly, the condensation product of acetone and phenylhydroxylamine yields a substance, m. p. 112°, having approximately the same composition. It is considered that the condensation product of acetone with arylhydroxylamines may be formed by condensation of 2 mols. of the primary additive compound and be represented by the formula  $\text{O} \begin{smallmatrix} \text{NR} \cdot \text{CMe}_2 \\ \diagup \diagdown \\ \text{NR} \cdot \text{CMe}_2 \end{smallmatrix} \text{O}$  or  $\text{O} \begin{smallmatrix} \text{NR} \cdot \text{CMe}_2 \\ \diagup \diagdown \\ \text{CMe}_2 \cdot \text{NR} \end{smallmatrix} \text{O}$ .

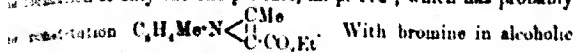
It is now found that the action of phenylhydroxylamine on ethyl acetoacetate leads to the formation of two isomeric products,  $\text{C}_{17}\text{H}_{21}\text{O}_3\text{N}$ , crystallising in white prisms, m. p. 120—121° and 121—122° respectively, which when treated with glacial acetic acid are transformed into a third isomeride crystallising in needles, m. p. 137°. A mixture of this with the isomeride, m. p. 136°, has m. p. 140°. When treated with bromine in alcoholic solution, the three isomerides form a mixture of mono- and di-bromo derivatives, m. p. 166°. The constitution of the condensation products of phenylhydroxylamine with ethyl

which may be stereoisomerides, is discussed. It is probable that the three substances are formed by way of an intermediate product,



which may undergo farther condensation in various directions.

The action of *p*-tolylhydroxylamine on ethyl acetoacetate leads to the formation of only the one product, m. p. 172°, which has probably



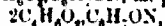
solution it yields a bromo-derivative,  $\text{C}_{13}\text{H}_{11}\text{O}_2\text{NBr}$ , m. p. 190°.

Diacetyl and benzylhydroxylamine form a white, crystalline *additive*

compound,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$ , m. p. 107.5°, which gradually decomposes to a very viscous oil, and is soluble in hot, but insoluble in cold, solvents;

decomposition may serve to characterise benzylhydroxylamine. With hydrogen chloride, phenylhydrazine, phenylcarbimide, and hydroxylamine, the additive compound gives the reactions of its components.

Benzylhydroxylamine forms two white, crystalline *additive* compounds with diacetyl:  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$ , m. p. 95°, and



m. p. 105°; the constitution of the former is represented by the formula  $\text{OH} \cdot \text{NPh} \cdot \text{CMe}(\text{OH}) \cdot \text{COMe}$ , but that of the latter, although suspected, remains undecided.

In the absence of a solvent, diacetyl and *p*-tolylhydroxylamine form a white, crystalline *additive* compound,  $2\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$ , m. p. 132°; in solution and cooled by ice an *isomeride*, m. p. 132°.

Diacetylhydroxylamine and diacetyl combine with slight development of heat, forming a viscous product. When heated with dilute mineral acids, the additive compounds of diacetyl and arylhydroxylamines are decomposed quantitatively into their components.

Methyl ethyl diketone reacts with  $\beta$ -substituted hydroxylamines with slight development of heat, forming unstable products. Attempts to form additive compounds of benzyl methyl diketone and benzyl  $\beta$ -substituted hydroxylamines were unsuccessful. (G. Y.)

#### Compounds of $\alpha$ -Naphthylcarbimide with Amino-Acids.

See NERNST and E. ROSENBERG (*Biochem. Zeitsch.*, 1907, 5, 106-107).—By shaking the alkaline solutions of amino acids with  $\alpha$ -naphthylcarbimide, the following compounds were obtained. With aspartic acid,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$ , m. p. 202°; with *d*-isoleucine,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$ , m. p. 192°; with *L*-aspartic acid,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$ , m. p. 115°; with *L*-asparagine,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$ , m. p. 199°; with *d*-phenylalanine,  $\text{C}_{20}\text{H}_{18}\text{O}_3\text{N}_2$ , m. p. 159—160°; with tryptophan,  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{N}_2$ , m. p. 159—160°; with *DL*-serine,  $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_2$ , m. p. 192°; with  $\delta$ -aminovaleric acid,  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{N}_2$ , m. p. 186°; with *DL*-leucylglycine,  $\text{C}_{19}\text{H}_{17}\text{O}_3\text{N}_2$ , m. p. 186°. The yield is usually 80—90%;  $\alpha$ -naphthylcarbimide derivatives can be prepared as the very stable silver or copper salts, and these can be isolated by ignition. (G. B.)

#### Analysis of Pine Tar. PETER KLASON, JOHN KÖHLER, and FRIEDRICH ARKIV. *Kem. Min. Geol.*, 1907, 2, No. 36, 1—31).

Methods and results of analysis of pine tars of various origins are given (compare *Stm. Abstr.*, 1900, i, 577) T. H. P.

**Red and White Isomeric Silver Salts of 2:4:6-Tribromophenol.** HERZ A. TOSNEY and WILLIAM H. HUNTER (*Ber.*, 1907, 40, 4332—4335).—Three methods are described for the preparation of a colourless silver 2:4:6-tribromophenoxide, of which the best is the following. The freshly precipitated red silver salt is dissolved in a small quantity of concentrated ammonium hydroxide, the solution diluted, and nearly neutralised with dilute sulphuric acid. On further dilution, the solution is treated with a concentrated solution of silver nitrate, whereby the pure white silver salt is generally precipitated. The red and the white varieties yield the same ethyl ester, and behave alike towards ethyl or methyl iodide in the absence of solvent, forming an amorphous substance, m. p. above 250° (decolor.), which does not contain iodine.

The authors propose the ordinary benzenoid formula for the white salt, and an ortho-quinonoid formula for the red,  $\text{OC}_6\text{H}_2\text{Br}_3\text{ONa}$ .

**Aminophenolsulphonic and Aminocresolsulphonic Acids.** II. 3-Nitro- and 3-Amino-*o*-cresolsulphonic Acids. GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4319—4322. Compare Abstr. 1906, 1030).—3-Nitro-*o*-cresol-5-sulphonic acid, prepared by heating 3-nitro-cresol with twice the quantity of concentrated sulphuric acid, crystallises with  $3\text{H}_2\text{O}$ . The sodium, potassium, barium, strontium, and calcium salts are described; those of the type  $\text{NO}_2\text{-C}_6\text{H}_3(\text{OH})(\text{SO}_3\text{M})_2$  are more coloured than those containing two equivalents of the metal. On reduction with hydrochloric acid and stannous chloride, the salt of 3-amino-*o*-cresol-5-sulphonic acid, which crystallises in needles containing  $\frac{1}{2}\text{H}_2\text{O}$ , and gives a deep red coloration with ferric chloride.

**Aminophenolsulphonic and Aminocresolsulphonic Acids.** III. 4-Nitro- and 4-Amino-*m*-cresol-6-sulphonic Acids. GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4322—4323).—4-Nitro-*m*-cresol and concentrated sulphuric acid at 70° yield, after four to six hours, 4-amino-*m*-cresol-6-sulphonic acid, which crystallises in needles. The sodium salt,  $\text{NO}_2\text{-C}_6\text{H}_3(\text{ONa})(\text{SO}_3\text{Na})_2\cdot 3\text{H}_2\text{O}$ , forms orange-yellow prisms. On reduction, the acid yields the corresponding amino acid.

**Aminophenolsulphonic and Aminocresolsulphonic Acids.** IV. Sulphonation of 3-Nitro-*p*-cresol. GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4324—4325).—3-Nitro-*p*-cresol is not attacked by concentrated sulphuric acid at the ordinary temperature, and is only exposed at higher temperatures. Fuming sulphuric acid attacks it into an acid,  $\text{C}_7\text{H}_5\text{O}_4$ , m. p. 128°, which forms an adduct,  $\text{C}_7\text{H}_5\text{O}_4\cdot\text{CO}_2\text{Et}$ , b. p. 265°, with an odour of melons, of which the corresponding phenylhydrazone has m. p. 96°, and the colourless semicarbazone m. p. 110°.

**2-Amino-1-methylphenylene-4:5-dithiol** [2-Amino-4:5-dithiol-toluene] and Sulphineazo-dyes. FRITZ FRÜHLICH, JAMES FRÜHLICH, and MAX JALON (*Ber.*, 1907, 40, 4420—4425. Compare Frühl. Frühl., this vol., i, 632).—In accordance with the view of the

and Mauthner (*Abstr.*, 1905, 1, 103), the introduction of two unsaturated groups in positions ortho to one another into a simple aromatic base as *o*-toluenesulpho- $\beta$ -naphthylamine, is found to confer on the compound the characteristic dyeing properties of sulphur dyes.

2-Nitro-4-sulphino-5-sulphonic acid is converted by Leuckart's method (*Abstr.*, 1890, 603) into potassium 4-sulpho-2-nitrotoluenesulphonate,  $C_6H_4O_2NS_2K, 1\frac{1}{2}H_2O$ , obtained as very small, light brown, needle-like crystals, decomposing above  $150^\circ$ . Hydrolysis by potassium carbonate results in the formation of the dipotassium salt of 6-nitro-*o*-toluenesulphonic acid,  $C_6H_4O_2NS_2K_2, 2H_2O$ , crystallising in small dark red prisms; a solution of the salt gives a light yellow precipitate with lead acetate. Both the solid salt and its aqueous solution are oxidised by atmospheric oxygen to the potassium salt of the corresponding disulphide,  $S_2[C_6H_4Me(NO_2)SO_2K]_2, 5H_2O$ , obtained as yellow needles, which is reduced by stannous chloride and converted into acid to the corresponding amine,  $S_2[C_6H_4Me(NH_2)SO_2H]_2$ , forming small, colourless crystals. The potassium salt of the nitro-sulphonate yields with phosphorus pentachloride the sulphochloride,  $[KMe(NO_2)SO_2Cl]_2$ , crystallising in light brown prisms, m. p.  $100^\circ$ , which on reduction is converted into 2-amino-4:5-dithioltoluene, a sulphochloride of which,  $C_6H_4NS_2HCl$ , is obtained as a white, crystalline powder; the lead salt is orange-red; the diethyl ether,  $(C_2H_5)_2N_2$ , is a thick oil, b. p.  $225-227/25$  mm.; its sulphate,  $(C_2H_5)_2N_2H_2SO_4$ , crystallises in long, colourless, silky needles.

2-Nitro-4:5-dithioltoluene is oxidised by the air with the formation of a substance,  $(C_6H_4NS_2)_2$ , obtained as an amorphous, yellow powder soluble in the common solvents.

2-Amino-4:5-dithiol- $\beta$ -naphthylamine 4:5-disulphide,  $C_{12}H_{12}N_2S_2$ , obtained by the action of  $\beta$ -naphthylamine to a diazotised solution of 2-amino-4:5-dithioltoluene as a dark red, amorphous powder, is insoluble in common solvents, but dissolves in an aqueous alkali sulphide solution, forming a dark red solution which dyes unmordanted cloth. The precipitate obtained on acidifying this solution is partially soluble in alcohol, from which solution after a time, on the addition of hydrogen peroxide, the disulphide separates; it is probable that the disulphide is reduced to the dithiol which dissolves.

W. H. G.

**Condensation of Aldehydes with Phenols.** Condensation of Quinol with Benzaldehyde and Formaldehyde. PAWEŁ, *Ann. J. Russ. Phys. Chem. Soc.*, 1907, 39, 1094-1103.—A summary of the work done so far on the subject is given, and it is pointed out that one criterion for judging the mode of reaction of aldehydes and phenols in the cases which do not comply with the usual rule has never been applied, namely, the determination of the molecular weights of the substances formed.

Quinol reacts with benzaldehyde, forming 3:6:3':6'-tetrahydroxy-*triphenylmethane*,  $CHPh[C_6H_3(OH)_4]_3$ , readily soluble in, but decomposed by, alkalis, dissolves in concentrated sulphuric acid, forming a dark red liquid, reduces Fehling's solution, and when heated at reduced pressure does not melt, but loses water and decom-



poses. Oxidising agents, such as chromic acid or hydrogen peroxide, also decompose it. When kept over phosphoric oxide, the substance  $\text{CHPh} \langle \text{C}_6\text{H}_4(\text{OH}) \rangle \text{O}$ , is formed, which, when exposed to air, is converted to the original compound.

The triacetyl derivative, possibly  $\text{CPhAc} \langle \text{C}_6\text{H}_4(\text{OAc}) \rangle \text{O}$ , is analysed readily, forming a brown, powdery substance,  $\text{C}_6\text{H}_4\text{O}_2$ , which decomposes on heating. The tribenzoyl derivative,  $\text{C}_6\text{H}_4\text{O}_2$ , is a light amorphous, pink powder, which turns dark red on heating and m. p. 220—240° (decomp.).

With formaldehyde, quinol forms 3:6:3':6'-tetrahydroquinolmethane,  $\text{CH}_2[\text{C}_6\text{H}_3(\text{OH})]_{2,2}$ , a light amorphous, brown powder, which decomposes on distillation at ordinary or reduced pressure, forming a small quantity of a colourless substance, m. p. 100—115°.

The diphenyl compound is very similar in properties to the triphenyl compound, but does not dissolve in sulphuric acid. With acetic anhydride, it forms a diacetyl derivative,  $\text{C}_{17}\text{H}_{16}\text{O}_6$ , a bright yellow amorphous substance similar in properties to the corresponding triphenyl derivative. (L.)

**Main Constituent of Japanese Lac.** RIKO MIYAMA and S. CHŌ (*Ber.*, 1907, 40, 4390—4393. Compare Yoshida, *Ann.* 1883, 43, 472; Tschirch and Stevan, *Abstr.*, 1906, i, 31; Miyama, *japanische Anstalt.*, 1906, No. 1000).—Urushic acid has the composition C 79.65 and H 9.75 after careful purification by absorption on petroleum; the "nitrogen" previously found in the acid was due to carbon monoxide (Miyama, *loc. cit.*). Dry distillation of urushic acid gives methane, hexane, hexylene, heptane, heptylene, octane, octylene,  $\text{C}_{11}\text{H}_{20}$ ,  $\text{C}_{14}\text{H}_{26}$ , and catechol, with small quantities of fatty acids and carbon dioxide. Oxidation with nitric acid gives a mixture from which oxalic, succinic, and suberic acids were isolated. Methylation of urushic acid gives a substance which has no longer phenolic reactions, is not hydrolysed by alcoholic potassium hydroxide, and is oxidised by nitric acid. Methoxyl determinations appear to show that about one-sixth of the oxygen is not methylated.

Urushic acid is readily acetylated and benzoylated, and these results show that urushic acid is a polyhydroxyphenol containing a large hydrocarbon grouping. (W.)

**Preparation and Properties of Trimethylenecarbinol and Propylcarbinol] and some of its Derivatives.** N. I. DENJANOFF and K. FORTUNATOFF (*Ber.*, 1907, 40, 4397—4402. Compare *Russ. Phys. Chem. Soc.*, 1907, 39, 1085—1094. Compare *Ann.* i, 1023).—Pure cyclopropylcarbinol was prepared by reducing cyclopropionate according to Bouveault and Blanc's method (*Ann.* 1904, i, 642), and has b. p. 123.2—123.4°/738 mm.  $n_D^{20}$  1.4313;  $n_D^{25}$  0.8995,  $n_D^{31}$  1.4313; the urethane forms needle-shaped crystals, m. p. 100—104°. With chromic acid, the alcohol yields the corresponding aldehyde,  $\text{CH}_2 \langle \text{CH} \rangle \text{COH}$ , b. p. 98°/734 mm.  $n_D^{20}$  1.4313.

14286, which yields a semicarbazone, m. p. 126°.

heating with hydrobromic acid causes the ring to break, and the alcohol is converted into a mixture of dibromides,  $\text{CH}_3\text{Me} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$ , together with  $\text{CH}_3\text{Me} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{Br}$  and  $\text{H} \cdot \text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$ . A small quantity of a monobromide,

$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$ , is also formed, and has b. p. 103°.

1-3740, D<sup>2</sup> 1-3600.

Z. K.

## Reaction of Substituted Phenyl Benzyl Ethers by Alkali.

A. A. AUWERS [add., in part, OTTO MAHLER] (*Annalen*, 1907, 857, 864) Compare Auwers and Rietz, this vol., i, 919).—Certain known substituted phenyl benzyl ethers (Auwers, Traub, and Welde, *Ber.*, 1907, 1, 168) are hydrolysed, not only by strong acids, but also, after gentle heating with alcoholic alkalis, or even when boiled with aqueous stannhydride. As Kumpf (Abstr., 1884, 1005) and Frische (*Mém.*, 1884, 1337) found that di- and tri-nitro-derivatives of phenyl and phenyl benzyl ethers are hydrolysed by alcoholic potassium carbonate, whereas the mono-nitro-derivatives and parent ethers remain unchanged, it seemed probable that the ease with which the various substituted ethers in question are hydrolysed depends on the substitution of the negative substituting groups. The authors have ascertained that, when boiled with alcoholic potassium hydride for three days, mono- and di-bromo-, dichloro-, and bromonitro-derivatives of phenyl benzyl ether, as also tribromo-derivatives having the bromine atoms distributed between the two benzene nuclei, remain unchanged, whereas under the same conditions 2:4:6 tribromo-, pentabromo-, and 2:4:6-trichloro-phenyl-, and 2:4:6 tri-iodo-*m*-tolyl benzyl ethers, as also 2:4-dichlorophenyl 4-nitrobenzyl ether, are respectively hydrolysed to the phenol and benzyl alcohol in one day at least. Since  $\psi$ -cumyl and dibromo- $\psi$ -cumyl benzyl ethers remain unchanged, the stability of phenyl benzyl ether is not diminished by the introduction of methyl groups.

The following substituted phenyl benzyl ethers are prepared by reacting the corresponding phenol with the benzyl chloride or bromide and sodium ethoxide in alcoholic solution.

*Bromophenyl benzyl ether*,  $C_{13}H_{11}OBr$ , slightly yellow oil, decomp.

distillation. *p*-Bromophenyl benzyl ether,  $C_{13}H_{11}OBr$ , rose coloured

p. 64-65. *o*-Bromophenyl *o*-bromobenzyl ether,  $C_{13}H_{10}OBr_2$ 

solid, which slowly crystallises, m. p. slightly above the ordinary

1. *p*-Bromophenyl *p*-bromobenzyl ether, small, white needles.

6. *Distillation*. *p*-Bromobenzyl *p*-bromobenzyl ether, oil, decomp. partially

11-14 4-Tribromophenyl benzyl ether, small, white needles.

2:4-Dibromophenyl benzyl ether, small needles, m. p.

2:4-Dibromophenyl p-bromobenzyl ether,  $C_{11}H_7OBr_3$ , long, white

needles, m. p. 93°. 2:4 Dichlorophenyl benzyl ether.

crystallizes in cubes, m. p. 61–62°, p. Bromo-o-nitro-

benzyl ether,  $C_{11}H_{16}O_2NBr$ , yellow needles, m. p. 84–85°.

3,4,5-Triisopropenyl benzyl ether,  $C_{17}H_{22}O$ , needles, m. p. 85°.

1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 2679, 26

*Pentabromophenyl benzyl ether*,  $C_{15}H_{11}OBr_5$ , white needles, m. p. 203—204°. *2:4:6-Trichlorophenyl benzyl ether*,  $C_{15}H_{11}OCl_3$ , white needles, m. p. 64—65°. *Tri-*tert*-m-tolyl benzyl ether*,  $C_{27}H_{35}O$ , white needles, m. p. 131°. *2:4-Dichlorophenyl p-nitrobenzyl ether*,  $C_{17}H_{13}O_2Cl_2$ , yellow needles, m. p. 148—150°. *Benzyl 2-nitro-4-chlorophenyl ether*,  $C_{15}H_{11}O_2Cl$ , prisms, m. p. 45°. *Benzyl dibromo-p-cumyl ether*,  $C_{15}H_{13}OBr_2$ , white needles, m. p. 110—111°. These ethers are readily and easily soluble in organic solvents.

**Base-forming Property of Carbon.** JAMES F. NORRIS (*Chem. J.*, 1907, 38, 627—642).—Norris and Franklin (ibid. i, 341) in discussing the properties of triphenylcarbinol suggest that by a change in the nature of the radicles, the basic properties of the compound could be increased to such a degree that a true organic base would be produced. The present investigation was undertaken with the object of studying this point.

When triphenylcarbinol is treated with cold hydrochloric acid (D 1.20), hydrobromic acid (D 1.49), or hydriodic acid (D 1.7), it is converted quantitatively into the corresponding triphenylcarbinyl halide.

Tri-*p*-tolylcarbinol has a greater basicity than the triphenyl compound, and is converted into the chloride by hydrochloric acid (D 1.12). It reacts with nitric acid (D 1.42) with formation of a nitrate,  $C(C_6H_4Me)_3 \cdot NO_3 \cdot 2HNO_3$ , whilst triphenylcarbinol is unaffected by this treatment. Triphenylcarbinol dissolves in concentrated sulphuric acid, and is reprecipitated on the addition of a small quantity of water. The tritolyl compound, however, dissolves in a mixture of equal volumes of sulphuric acid and water, and forms a sulphate,  $C(C_6H_4Me)_3 \cdot HSO_4 \cdot H_2SO_4$ , which forms deep orange-coloured silky needles.

The compounds obtained from triphenylcarbinol behave as true salts. A solution of the chloride in acetone has electrolytic conductivity, and, when a direct current is passed through the solution, a substance, probably analogous to triphenylmethyl, is deposited at the cathode. On adding silver nitrate to a solution of the chloride in acetone, silver chloride is precipitated. The chloride is decomposed by strong sulphuric acid with formation of the sulphate and evolution of hydrogen chloride. It reacts with alcohol, thus:  $C(C_6H_4Me)_3 + EtOH \rightleftharpoons C(C_6H_4Me)_3 \cdot OEt + HCl$ .

Benzyl alcohol can be converted into the chloride, bromide, or iodide by concentrated solutions of the halogen acids.

The behaviour of alcohols of the paraffin series under the above conditions has been studied. *tert*-Butyl alcohol, when treated with concentrated hydrochloric acid, gives a quantitative yield of the chloride at the ordinary temperature. Usually, however, it is necessary to employ heat to bring about the reaction between alcohols and acids, and for this reason the mixtures of acids and water of constant boiling point have been used. In this way, yields of 91% and 89% were obtained of *tert*-butyl bromide and iodide respectively, and 95% of *sec*-butyl iodide.

When *sec*-butyl alcohol was distilled with concentrated hydrochloric

hydrogen chloride, the chloride was not produced, but, on using the acid of constant boiling point, a yield of 80% was obtained. The primary alcohols are not converted into the chlorides when distilled with pyridine-acetic acid.

This method is recommended for the preparation of alkyl bromides and iodides. On slowly distilling a mixture of the alcohol with a large excess of the acid of constant b. p., the halide passes over and remains in the early fractions. The product is shaken with concentrated hydrochloric acid to remove unchanged alcohol, and is afterwards dried and distilled. Excellent yields of methyl, ethyl, propyl, isopropyl, iso-, sec-, and *tert*-butyl, isobutyl, and allyl bromides and iodides have been obtained in this way. R. G.

**A Vinyl Alcohol of the Type  $C_6H_5CH=CH-OH$ .** MARC TIFFENEAU and PIERRESENNE (*Compt. rend.*, 1907, 145, 628—631).—The alcohol obtained from estragole dibromide by the successive action of alcoholic potassium acetate and potassium hydroxide is  $\beta$ -anisyl- $\beta$ -methylvinyl alcohol  $OMe \cdot C_6H_4 \cdot CMe:CH-OH$ , and not anisylcyclopropanol as previously described (this vol., i, 515). This alcohol, b. p. 154—155°/12 mm., is stable in neutral or alkaline medium, and is converted into anisylhydratropaldehyde by distillation under ordinary pressure, or by action of dilute acids, or when preserved in a vacuum over concentrated sulfuric acid. The methyl ether,  $OMe \cdot C_6H_4 \cdot CMe:CH-OMe$ , b. p. 134—135°/12 mm.,  $D_4^{20}$  1.073,  $D_4^{25}$  1.0615, is identical with the ether obtained by action of yellow mercuric oxide on the methylidohydrin of estragole (Tiffeneau, this vol., i, 922); the acetyl derivative has b. p. 175—176°/13 mm., or 288° under ordinary pressure,  $D_4$  1.123,  $n_D^{20}$  1.5409. M. A. W.

**The Solubility of Castor Oil in Lipoids.** WILHELM FIEBENNE (*Ann. Chem. Physiol. Path.*, 1907, 10, 299—311).—The solubility of castor oil, cholesteryl stearate, in olive oil, oleic acid, castor oil, myristic acid, ricinoleic and crotonoleic acids has been determined by the methods of (1) melting point, (2) specific gravity, and (3) refractive index. Similarly, the solubilities of the oils and acids in the esters have been determined. J. J. S.

**A Phytosterol from Echinophora spinosa.** J. TARROURIECH and HENRI DUBOIS (*Chem. Zentr.*, 1907, ii, 969—970; from *Bull. Sci. Pharm.*, 1907, 14, 387—392).—The fatty substances obtained from the roots of *Echinophora spinosa* yield on hydrolysis a *phytosterol* crystallising in white, orthorhombic plates, m. p. 148°. The following derivatives were prepared: *benzoate*, m. p. 145°; *acetate*, pearly-white plates, m. p. 124—125°; *propionate*, crystallising from alcohol in plates, m. p. 109—110°, but when precipitated by alcohol from a carbon tetrachloride solution, m. p. 105°. W. H. G.

**Production of Phenolic Acids by Oxidation of Ammonium Salts of Benzoic Acid.** HENRY D. DAKIN and MARY DOWS HERTER (*Ind. Chem.*, 1907, 3, 419—434).—Hydrogen peroxide, acting on the ammonium salts of benzoic acid or its chloro-, bromo-, nitro-, and amino-

derivatives, can introduce hydroxyl groups into the nucleus, but the yield of phenolic acid is small. Hippuric acid undergoes further oxidation with difficulty. Benzoic acid yields *o*-, *m*-, and *p*-hydroxybenzoic acids in about equal amount; on further oxidation, the *ortho*-hydroxybenzoic acids yield protocatechuic (3:4-dihydroxybenzoic) acid, while the *meta*-hydroxybenzoic acid yields 2:3-dihydroxybenzoic acid. Thus the second hydroxyl group takes up a position *ortho* to that already in the ring. A part of the benzoic acid is oxidized to carbon dioxide, and probably other products are also formed. The reaction occurs in approximately neutral solutions, and to some extent at the ordinary temperature. The possible origin of phenolic substances in animal and vegetable tissues is considered, and although there is ample proof of their origin by the oxidation of preformed aromatic substances, there is little evidence at present that they originate directly from the condensation or rearrangement of a special substances. W. L. H.

***m*-Toluic Acid.** VICTOR JÜRGENS (*Ber.*, 1907, 40, 4492-4493). It has been shown by Findelee (Abstr., 1906, i, 43) and Knebel (Abstr., 1904, i, 619) that phthalylglycine esters containing a methoxy- or ethoxy-radicle in position 4, undergo the same transformation as phthalylglycine ester, being converted by sodium methoxide into quinoline derivatives (compare Gabriel and Colman, Abstr., 1906, i, 944). In order to see if phthalylglycine esters substituted in position 3 undergo a similar change, 3-methylphthalylglycine anhydride has been prepared and its behaviour towards sodium methoxide investigated; it is found to undergo no such transformation.

Several of the following new compounds were obtained in successful attempts to prepare 3-methylphthalic acid (compare Young, Abstr., 1892, 1221); the acid was finally obtained from methyl 2-*m*-toluate (compare Findelee, Abstr., 1906, i, 21) by reduction to *m*-aniline, replacement of the amino-group by the cyano-group and subsequent hydrolysis of the cyano-derivative.

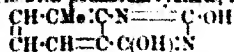
2-Nitro-*m*-toluic acid, when treated with phosphorus pentoxide and subsequently with ammonia, is converted into the amide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{NH}_2$  [2:1:3], m. p. 192°; this compound is heated with phosphoric oxide yields 2-nitro-*m*-toluonitrile,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{CN}$ , crystallising in needles, m. p. 84°. The alcoholic ammonium sulphide on the latter compound leads to the formation of 2-amino-*m*-toluamide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 60°.

Methyl 2-nitro-*m*-toluate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{Me}$ , m. p. 74°, yields on reduction with tin and hydrochloric acid, the crystalline hydrochloride of methyl 2-amino-*m*-toluate,  $\text{C}_8\text{H}_{11}\text{O}_2\text{N} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ; the free base is a viscous oil with an odour like orange-peel. It is converted on oxidation and treatment with cuprous cyanide into methyl 2-cyano-*m*-toluate,  $\text{CN} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{Me}$ , crystallising in long, white, prismatic needles, m. p. 68–70°. This compound is hydrolysed by hydrazine acid to 3-methylphthalic acid; the imide, m. p. 187°, and anhydride, m. p. 114–115° (Young gives m. p. 109–110°), were prepared. 3-Methylphthalylglycine,  $\text{C}_8\text{H}_7\text{MeO}_2\text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , resulting from the interaction of glycine and 3-methylphthalic anhydride, crystallises in white, felted needles, m. p. 195°; the methyl ester, m. p. 130°.

and finally, undergoes no transformation when treated with sodium

hydroxide. *Formyl-L-phenylalanine*, m. p. 173°, the methyl ester of which is

crystalline, reacts with potassium cyanate, forming 2:4-dihydroxy-



a crystalline substance, m. p. 283°. It is converted by phosphorus pentachloride into

8-methyl-8-methylquinazoline,  $\text{C}_9\text{H}_9\text{N}_2\text{Cl}$ , crystallising in fine,

white, leaf-like flakes, m. p. 140°. The latter compound is reduced by

nitric acid to 8-methyldihydroquinazoline,  $\begin{array}{c} \text{CH} \cdot \text{CMe} : \text{CN} \rightleftharpoons \text{CH} \\ | \\ \text{CH} \cdot \text{CH} = \text{C} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$

prismatic crystals, m. p. 112°. The *chromate*, *aurochloride* and *platinichloride*,  $(\text{C}_9\text{H}_9\text{N}_2)_2\text{H}_2\text{PtCl}_6$ , are well-defined, crystalline substances.

W. H. G.

**Synthesis of Polypeptides. XXII. Derivatives of *L*-Phenylalanine.** EMIL FISCHER and WALTER SCHOELLER (*Annalen*, 1907, 357,

246). Polypeptides derived from optically active phenylalanine have not been prepared previously because of the difficulty of obtaining the active amino-acids. *r*-Phenylalanine has now been resolved into its active components by means of the formyl derivative (compare Fischer and Warburg, *Abstr.*, 1906, i, 72). Whilst glycyl-*L*-phenylalanine is obtained by the action of chloroacetyl chloride on *L*-phenylalanine, *L*-phenylalanylglycine is prepared by the action of ammonia on  $\alpha$ -bromohydrocinnamoylglycine, which is formed from *d*-phenylalanine by way of *d*- $\alpha$ -bromohydrocinnamic acid (Fischer and Carl, *Abstr.*, 1906, i, 27) and *d*- $\alpha$ -bromohydrocinnamoyl chloride. These two peptides yield the same anhydride.

*Formyl-L-phenylalanine*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ , prepared by heating *r*-phenylalanine with formic acid on the water bath, crystallises from water in microscopic plates, softening at 165.5° (corr.), m. p. 168.8–169.8° (corr.), when heated with brucine and methyl alcohol, it dissolves and on cooling deposits the *brucine* salt of the *d*-compound,

which, on hydrolysis, yields *formyl-D-phenylalanine*,  $[\alpha]_D^{20} - 75.43^\circ$

( $\pm 0.2^\circ$ ). The *brucine* salt of the *L*-compound, obtained from the methyl alcohol filtrate, yields *formyl-L-phenylalanine*,  $[\alpha]_D^{20} + 75.2^\circ$

( $\pm 0.2^\circ$ ). The optically active formylphenylalanines crystallise from water in plates, soften at 163° (corr.), m. p. 167° (corr.), and are

quite more soluble than the *r*-compound. The optically active

hydrobromides are prepared by boiling the formyl derivatives with

hydrobromic acid and treatment of the resulting hydrobromides

with ammonia. *d*-Phenylalanine prepared in this manner has m. p. 163° (corr.) (decomp.),  $[\alpha]_D^{20} + 35.14^\circ (\pm 0.5^\circ)$  (Fischer and Mounoyrat,

*Abstr.*, 1900, i, 647), and has a sweet taste. *L*-Phenylalanine, m. p. 165° (corr.) (decomp.),  $[\alpha]_D^{20} - 35.09^\circ (\pm 0.5^\circ)$  ( $[\alpha]_D^{18} - 38.1^\circ$  to  $-40.2^\circ$ ;

Saenger and Winterstein, *Zeitsch. physiol. Chem.*, 1902, 36, 299), has a bitter taste, and when heated with formic acid yields the formyl

derivative,  $[\alpha]_D^{20} + 72.4^\circ$ .

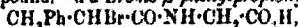
$\alpha$ -Bromohydrocinnamic acid, prepared by the action of nitric

acid on *d*-phenylalanine hydrobromide in hydrobromic acid in

presence of bromine at  $-10^{\circ}$ , or in a more impure state by the action of sodium nitrite on *d*-phenylalanine hydrobromide in 40% hydrobromic acid solution cooled by ice, has  $[\alpha]_D^{25} +9^{\circ}$ , and contains therefore about 13% of its optical isomeride. In the same manner, *l*-leucine hydrobromide on treatment with sodium nitrite in 47% hydrobromic acid solution yields *l*-*a*-bromoisobutyric acid containing about 22% of the *d*-acid.

*l*-Phenylalanine ethyl ester hydrochloride, prepared by the action of hydrogen chloride on *l*-phenylalanine in alcoholic solution, crystallises in long, colourless needles,  $[\alpha]_D^{25} -7.6^{\circ} (\pm 0.3^{\circ})$ . On treatment with hydrobromic acid and bromine, the *l*-ester forms a dark red oil, and on treatment with nitric oxide in cooled hydrobromic acid solution yields an impure ethyl *d*-*a*-bromohydrocinnamate, b. p.  $110^{\circ}/0.35$  mm.,  $[\alpha]_D^{25} +2^{\circ}$ . Ethyl *l*-*a*-bromohydrocinnamate, prepared by esterification of a specimen of the *l*-acid containing 18% of the *d*-acid, has  $[\alpha]_D^{25} -15.5^{\circ}$ . Here, the pure *l*-acid has  $[\alpha]_D^{25}$  about  $-24^{\circ}$ , and Walden's transformation does not take place in the formation of ethyl *a*-bromohydrocinnamate by the action of bromine and nitric oxide on *l*-phenylalanine ester.

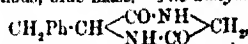
*d*-*a*-Bromo- $\beta$ -phenylpropionyl chloride, prepared in an 80% yield from *d*-*a*-bromohydrocinnamic acid,  $[\alpha]_D^{25} +9^{\circ}$ , is obtained as a colourless oil, b. p.  $90^{\circ}/0.25$  mm., has a suffocating odour, and contains at least 25% of the *r*-compound, *d*-*a*-Bromo- $\beta$ -phenylpropionylglycine



obtained by the action of the chloride and sodium hydroxide on glycine and extraction of the product with ether, crystallises on addition of light petroleum to the ethereal solution in long needles, m. p.  $115-146^{\circ}$  (corr.),  $[\alpha]_D^{25} -14.65^{\circ} (\pm 0.3^{\circ})$ . The portion of the product insoluble in ether is the *r*-compound. On treatment with aqueous ammonia, the *d*-compound yields *l*-phenylalanylglycine  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which crystallises in needles, commences to sinter at about  $219^{\circ}$  (corr.), m. p.  $224^{\circ}$  (corr.) (decolor.),  $[\alpha]_D^{25} +54.20^{\circ} (\pm 0.4^{\circ})$ , or after precipitation by addition of alcohol to the aqueous solution and drying at  $80^{\circ}$  over phosphoric oxide in a vacuum,  $[\alpha]_D^{25} +53.63^{\circ} (\pm 0.4^{\circ})$ , and has a bitter taste; the aqueous solution has a slight acid reaction, and when boiling dissolves copper oxide, becoming blue.

Chloroacetyl-*l*-phenylalanine,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , softens at about  $123^{\circ}$  (corr.), m. p.  $136^{\circ}$  (corr.),  $[\alpha]_D^{25} +51.25^{\circ} (\pm 0.4^{\circ})$ , or after recrystallisation from water,  $[\alpha]_D^{25} +51.80^{\circ} (\pm 0.3^{\circ})$ .

Glycyl-*l*-phenylalanine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , crystallises in colourless needles, m. p.  $267^{\circ}$  (corr.) (decolor.),  $[\alpha]_D^{25} +4.1^{\circ} (\pm 0.6^{\circ})$ , or after recrystallisation from water,  $[\alpha]_D^{25} +42.0^{\circ} (\pm 0.4^{\circ})$ , has a bitter taste, forms a slightly acid aqueous solution, and gives a blue solution when boiled with water and copper oxide; the neutral salt forms an amorphous, blue mass. The anhydride,

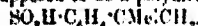


formed from *l*-phenylalanylglycine or glycyl-*l*-phenylalanine by conversion into the methyl ester and treatment of this with alcoholic ammonia, crystallises in needles, m. p. about  $265.5^{\circ}$  (corr.) (decolor.).

$+0.5^{\circ}$  ( $\pm 0.4^{\circ}$ ), or after recrystallization from water,  $+0.5^{\circ}$  ( $\pm 0.5^{\circ}$ ). G. Y.

**The Liberation of Carbon Monoxide from the Simplest Aliphatic Acids, Trimethylacetic (or Dimethylpropionic) and Methylmethylacetic [ $\alpha$ -Phenyl- $\alpha$ -methylpropionic] Acids.** BISTRITZKI and LOUIS MAURON (*Ber.*, 1907, 40, 1775. Compare Abstr., 1901, i, 701; 1904, i, 44, 315; 1905, i, 135).—It has been shown already that triphenylacetic acid, on dissolution in sulphuric acid, gives triphenylcarbinol, and carbon monoxide is eliminated quantitatively. On treating aliphatic aliphatic acids similarly, carbon monoxide is again liberated quantitatively, but in these cases no carbinol is formed, the corresponding aldehyde being obtained. The investigation has been extended to methylmethyl- and trimethyl-acetic acids. In these cases also, carbon monoxide is evolved quantitatively, but neither olefine nor alcohol is obtained. The elimination of carbon monoxide proceeds in the most case, and is most complete, in the case of tertiary acids, and not readily with monobasic primary acids, the secondary acids occupying an intermediary position.

$\alpha$ -Phenyl- $\alpha$ -methylpropionic acid (m. p.  $80-81^{\circ}$ ; Wallach, *Nach. Wiss.*, 1899, 126, gives  $77-78^{\circ}$ ), on dissolution in sulphuric acid and heating for thirty minutes at  $60-70^{\circ}$  after being kept for thirty minutes on neutralisation of the aqueous solution with barium hydroxide, the barium salt of polymerised ( $\beta$ )  $\alpha$ -methylstyrenesulphonic acid,  $(C_9H_7SO_3)_n \cdot Ba_6H_4O_2$ , crystallising in microscopic prisms; the potassium salt,  $(C_9H_7SO_3K)_n$ , forms slender, silky needles. It is very slowly hydrolysed by acids, and is therefore not an ester of sulphuric acid, and is supposed to be a polymeride of



$\alpha$ -Dimethylpropionic acid, when heated with sulphuric acid at  $100-110^{\circ}$  for three to four hours, yields isobutylene disulphonic acid,  $(C_4H_7SO_3)_n$ , in 35% yield as potassium salt,  $(C_4H_7SO_3K)_n$ , crystallising in needles. The ammonium salt,  $(C_4H_7SO_3NH_4)_n$ , forms plates, decomp. at  $250^{\circ}$ ; the lead salt,  $C_4H_7SO_3Pb \cdot 2H_2O$ , large, rectangular plates, m. p.  $62-64^{\circ}$ , prepared from the lead salt, forms hexagonal plates, m. p.  $62-64^{\circ}$ , and is not hydrolysed. Further, it behaves like an unsaturated substance towards bromine water and potassium permanganate. It may have either of the four possible formulae:  $(C_4H_7SO_3H)_n$ ,  $SO_3H \cdot CH \cdot CMe \cdot CH_2 \cdot SO_3H$ ,  $CMc_2 \cdot C(SO_3H)_2$ ,  $C(CMe) \cdot CH(SO_3H)_2$ . W. R.

**General Reaction for Differentiating between Multiple Linkings in Unsaturated Compounds of the Aromatic and Aliphatic Series.** ERRORE MOLINARI (*Ber.*, 1907, 40, 1641-1651).—Ozone is quantitatively absorbed by compounds containing double linkings in the proportion of 1 mol. of ozone for each double linkage, ozonides being formed; compounds, on the other hand, containing triple linkings do not absorb ozone. With benzenoid derivatives, where in the ring there is no "true" double linkage, no ozone is absorbed; with those benzenoid derivatives which contain a true double linkage, ozone is absorbed.



The behaviour of ozone towards *stearolic acid*, *phenylpropionic acid*, and *o-nitrophenylpropionic acid* was studied.

With aromatic compounds, the author draws the conclusion that if a given substance does not take up ozone, the centric formula should be assigned to the compound in question; if ozone is absorbed, the compound contains "true" double linkings. The following compounds absorb much ozone: resorcinol, quinol, phloroglucinol, pyrogallol, *p*-benzoquinone, cinnamic acid, phenanthrene, anthracene, azobenzene, aminoazobenzene, benzidine, naphthalene,  $\alpha$ -naphthylamine,  $\beta$ -naphthylamine, and quinoline. The following compounds do not absorb ozone: benzene, toluene, the xylenes, nitrobenzene, p-tolene, hydrocinnamic acid, phenylpropionic acid, *o*-nitrophenylpropionic acid, diphenyl, benzophenone, diphenylmethane, fluorene, phthalan, quinone, azobenzene, naphthaquinone, anthraquinone, pyridine, and a quinoline. Phenol and catechol absorb small quantities.

From the behaviour of benzene with ozone, the author concludes that the centric formula should be assigned to it, since benzene and ozone scarcely interact; this is opposed to the experience of Harries.

A. M. K.

**Esters of Hydroaromatic Amino-carboxylic Acids.**—A. K. SKITA (*Ber.*, 1907, 40, 4167—4182).—The object of this investigation was to ascertain if the substances are similar to the aliphatic amino-esters, to study *cis*- and *trans*-isomerism, and also to see if the property of local anaesthesia, possessed by ethyl aromatic  $\beta$ -amino-carboxylate was characteristic of similar hydroaromatic compounds.

The compounds examined were all 4-aminocarboxylates. For isophoroncarboxylate (ethyl 2:6:6-trimethylcyclo  $\Delta^2$ -hexene-1-carboxylate) was prepared by the patented method (D.R.P. 115,555. Compare also Abstr., 1905, i, 349). When left in a methyl alcohol solution of hydroxylamine hydrochloride for eight days, and the solvent then distilled, *ethyl oximinoisophoroncarboxylate hydrochloride* was obtained in needles, m. p. 125°. The sodium salt of the oxime is hydrolysed by water; the oxime,  $C_{12}H_{19}O_3N \cdot \frac{1}{2}H_2O$ , crystallises from dilute alcohol in slender needles, m. p. 78°. The oxime behaves differently towards various reducing agents. With sodium amalgam in alcohol, a 46% yield of *ethyl cis-4-amino-2:6:6-trimethylcyclohexene-1-carboxylate*,  $C_{12}H_{21}O_2N$ , is obtained as an oil, b. p. 124—125° (There is also a small fraction, b. p. 118—120°/9 mm., and 1% of crude oil remains behind.) The *platinichloride*,  $C_{12}H_{21}O_2N \cdot 2PtCl_3$ , decomps. 248°; the *hydrogen citrate*,  $C_{20}H_{29}O_{11}N_2$ , forms hygroscopic crystals; the normal *citrate*,  $C_{12}H_{17}O_{13}N_2$ , is very hygroscopic. When the ester is boiled with sodium ethoxide for four hours and the alcohol removed, a *lactam*,  $C_{10}H_{15}ON$ , is obtained, crystallising from acetone in needles, m. p. 138—139°, b. p. 159—160°/10 mm. Not only have the elements of alcohol been lost, but also the hydrogen atoms as well. This lactam formation shows the compound to be the *cis*-compound and to have the amino group. Ethyl isophoroncarboxylate and aminoisophoronate, when heated in a sealed tube at 200° for five hours, give

the tartrate of the amino-ester, and this on hydrolysis with 30% sodium hydroxide yields the *cis*-modification.

Ethyl oximinophosphonocarbonylate, when treated with six times the theoretical amount of sodium amalgam in alcohol and acetic acid, gives an oil. On fractional distillation is separated into two main fractions: (1) b. p. 127—130°/9 mm., solidifies on cooling; (2) b. p. 130—133°, and does not solidify. Both have the composition,  $C_{11}H_{21}O_5$ , of *ethyl dihydroisophosphonocarbonylates*; the two forms are probably derived from the ethylenic linkings becoming reduced.

The action of ethyl dihydroisophosphonocarbonylate (b. p. 148—150°) on sodium reduction with sodium amalgam or with ammonium formate gives the *cis*-modification.

*Ethyl trans 4-amino-2:6:6-trimethylcyclohexane-1-carboxylate*,  
 $C_{15}H_{27}O_2N$ ,

obtained by the reduction of ethyl oximinophosphonocarbonylate with sodium and alcohol, is an oil, b. p. 127—128°/11 mm., and is unchanged on twelve hours' boiling with sodium ethoxide solution. The *hydrochloride*,  $C_{15}H_{27}O_2NCl$ ; *tartrate*,  $C_{30}H_{52}O_{12}N_2$ , and *platinichloride*,  $(C_{15}H_{27}O_2N)_2Pt$ , decomp. 279°, have been prepared.

A heavier fraction, b. p. 150—160°/11 mm., obtained during the reduction consists of a *bimolecular ethyl aminotrimethylcyclohexanecarbonylate*,  $C_{30}H_{52}O_5N_2$ , and the solid ethyl dihydroisophosphonocarbonylate has also been isolated.

On the reduction of the ethyl oximinophosphonocarbonylate with sodium and methyl alcohol, a *lactimide-carboxylate*,  $C_{16}H_{27}O_5N$ , is obtained, crystallising from acetone in slender, white needles, m. p. 124°, b. p. 125°/8 mm. Hydroxylamine is not liberated from the action of hydrochloric acid.

*Ethyl 4-Hydroxy-2:6:6-trimethylcyclohexane-1-carboxylate*,  $C_{15}H_{27}O_3$ , obtained by the action of nitrous acid on the corresponding amino-ester, is an oil, b. p. 144—148°/12 mm. Another substance named is ethyl cyclogeraniolenecarbonylate,  $C_{17}H_{29}O_2$ , b. p. 87—88°/10 mm., due to removal of the elements of water (D.R.P. 148080).

The *oxime hydrochloride* of ethyl dimethylcyclohexanonecarboxylate,  $C_{12}H_{21}O_2NCl$ , has m. p. 115°; the oxime itself is oily. Its reduction by sodium amalgam and acetic acid in the presence of sodium ethoxide yields the corresponding amino-ester,  $C_{11}H_{21}O_2N$ , an oil, b. p. 118—121°/10 mm., which has been characterised by preparing the *platinichloride*,  $(C_{11}H_{21}O_2N)_2Pt$ , decomp. 250°, and the *citrate*,  $C_{30}H_{51}O_{12}N_3$ . This ester is a *cis* form, because with sodium ethoxide it gives an oil, b. p. 158—160 mm., which is apparently a lactam or mixture of esters.

A physiological examination of the tartrates and citrates show them to be analogous to the aromatic amino-acids in possessing the property of local anaesthesia.

W. R.

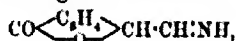
**Preparation of Glyceryl Salicylate.** CARL SORGER (D.R.P. 251111)—Glyceryl monosalicylate,  $C_9H_{11}(OH)_2O\cdot CO\cdot C_6H_4\cdot OH$ , is easily obtained by heating methyl or ethyl salicylate with glycerol containing a trace of sodium hydroxide or some salt of sodium; the temperature is gradually raised to 220° and maintained until methyl or ethyl

alcohol ceases to distil off. The glyceryl ester crystallises from ether in white needles.

**Barium *p*-Hydroxybenzoate.** WILLIAM OCHSENER DE COCKEN (Bull. Acad. roy. Belg., 1907, 711—713. Compare this vol., i, 445). This salt dissolves easily in water, and the specific gravities of a number of solutions of different strengths are tabulated in the original. Unlike calcium *p*-hydroxybenzoate, it does not exhibit triboluminescence. The calcium salt dissolves easily in alcohol, but the barium salt is soluble with difficulty in this solvent, as the solution becomes turbid on standing, depositing a mixture of the anhydrous and monohydrated salts. A solution of calcium *p*-hydroxybenzoate in alcohol, on the contrary, remains clear indefinitely.

Barium *p*-hydroxybenzoate does not dissolve in, and is not appreciably acted on by, either ethyl formate or acetate. I. A. H.

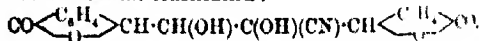
**$\omega$ -Bromoacetophenone- $\delta$ -carboxylic Acid.** SIDONIE GRILLÉ (Ber., 1907, 40, 4227—4239. Compare this vol., i, 241—242).  
methylenephthalide,  $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{O} \end{array} \text{CH} \cdot \text{CH} \cdot \text{NH}_2$ , or



prepared by the action of ammonia on methyl  $\omega$ -bromoacetophenone-carboxylate in presence of alcohol, crystallises from alcohol in large quadratic leaflets, m. p. 176—178°, and is transformed into the same m. p. 154—155°, of hydroxymethylenephthalide (loc. cit.) by the action of hydroxylamine. When treated with concentrated hydrochloric acid at 0°, aminomethylenephthalide is converted into hydrazomethylenephthalide and an isomeric amino-compound,  $\text{C}_8\text{H}_7\text{O}_3\text{N}_2$ , which separates from alcohol in oblong plates, sintering at 200°, m. p. 217°, and is also obtained by the action of aqueous ammonia on  $\omega$ -bromoacetophenone- $\delta$ -carboxylic acid.

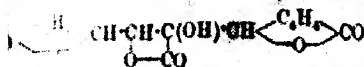
**$\omega$ -Aminoacetophenone- $\delta$ -carboxylamide**,  $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$ , obtained by the action of aqueous ammonia on methyl  $\omega$ -bromoacetophenone- $\delta$ -carboxylate, separates from acetone in glistening crystals resembling whetstone, m. p. 144—145° (decomp.), is soluble in water, forms a crystalline hydrochloride, hydrobromide, and picrate (m. p. 214—215°), but yields no precipitate with auric or platinum chloride. In the same reaction is formed a compound,  $(\text{C}_8\text{H}_7\text{O}_3\text{N}_2)_2$ , which crystallises from aniline in bundles of orange-red, flat needles, m. p. 140° (decomp.).

To the compound,  $\text{C}_8\text{H}_{13}\text{O}_6\text{N}$ , m. p. 223°, formed by the action of potassium cyanide on  $\omega$ -bromoacetophenone- $\delta$ -carboxylic acid, the author ascribes the constitution:



which is supported by the following transformations. When treated with dilute sodium hydroxide solution, it yields hydroxymethylene-

phthalide, methylenephthalide. When treated with cold concentrated hydrochloric acid or heated with 50% acetic acid, it is converted into the *trilactone*, which



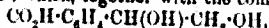
separates in oblique-ended prisms or six-sided plates, m. p. 245°, and becomes Feuling's solution when dissolved in alkali.

The action of dilute potassium hydroxide solution on this trilactone, hastened by the addition of excess of hydrochloric acid, yields: (1) the *lactonic acid*,  $\text{C}_{10}\text{H}_{10}\text{O}_6$ , which crystallises in oblique-ended prisms, melting at 180°, m. p. 199–200°; this lactonic acid is formed by the partial action of the two end lactonic rings, and, when heated with water, yields a lactone, separating in colourless, cubical crystals, m. p. 121–124°, which is isomeric with the trilactone, m. p. 245°, and termed the *isolactone*; the  $\alpha$ -lactonic acid yields a sparingly soluble ammonium salt,  $\text{C}_{10}\text{H}_{10}\text{O}_6 \cdot \text{NH}_4$ , m. p. 188°, and a still less soluble cesium salt; (2) the  $\beta$ -lactonic acid,  $\text{C}_{10}\text{H}_{10}\text{O}_6$ , separating as a crystalline powder, which froths at 180°, forming a pale yellow, turbid mass which becomes clear at 190°; it is readily soluble in water or alcohol, and, when treated with glacial acetic acid, loses water, giving the *anhydride*, m. p. 245°; the *silver salt*,  $\text{C}_{10}\text{H}_{10}\text{O}_6 \cdot \text{Ag}$ , of the  $\beta$ -lactonic acid was prepared.

When the trilactone, m. p. 245°, is treated with an excess of cold potassium hydroxide solution and the solution subsequently acidified with glacial acetic acid, it yields the  $\alpha$ -lactonic acid and an isomeric *lactonic acid*,  $\text{C}_{10}\text{H}_{10}\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ , m. p. varying from 188–189° to 200–205°, according to the rapidity of heating; this  $\gamma$ -acid forms a *barium silver salt*,  $\text{C}_{10}\text{H}_{10}\text{O}_6 \cdot \text{Ag}$ , and is converted by concentrated acetic acid into the original trilactone, m. p. 245°. When the latter is heated in a closed flask with about three equivalents of dilute acetic hydroxide, it yields the *barium salt*,  $(\text{C}_{10}\text{H}_{10}\text{O}_6)_2 \cdot \text{Ba}_2$ , of the  $\gamma$ -lactonic acid.

$\text{CO}_2\text{H}-\text{C}_6\text{H}_4-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{C}(\text{OH})(\text{CO}_2\text{H})-\text{CH}(\text{OH})-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ , which could, however, not be obtained in the free state, the barium salt giving the  $\beta$ -lactonic acid when treated with dilute sulphuric acid.

When heated with dilute barium hydroxide solution, the trilactone, m. p. 245°, is converted into formic and phthalidecarboxylic acids (m. p. 152°), which, together with the compound,



are the expected products of the tribasic acid referred to above.

When heated with phosphorus pentachloride, the trilactone loses water, yielding the compound,  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , which crystallises from acetic acid in colourless, quadratic or oblong plates, sintering at 240°, m. p. 260–262°; the constitution of this compound is to be investigated.

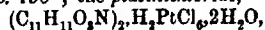
T. H. P.

**Derivatives of Imides of Dibasic Acids.** PAUL MENDELSSOHN (*Ann. Chem. Phys.*, 1907, 40, 4400–4408).—The transformation of trimethylene-phthalimide into the  $\beta$ -hydroxy-compound is shown to take place through the same intermediate stages as in the case of the *isobutyric* compound (compare Gabriel, *Abstr.*, 1905, i, 649).

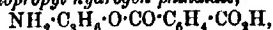
*β*-Bromopropylphthalamic acid,  $C_8H_8Br \cdot NH \cdot CO \cdot C_6H_4 \cdot CO \cdot H$ , prepared by the action of alcoholic potassium hydroxide on *β*-bromopropylphthalimide, crystallises in rhombic plates, m. p. 126°. The

ino-base,  $C_8H_8 \begin{matrix} CO \cdot NH \cdot CH_2 \\ CO \cdot O \cdot CHMe \end{matrix}$ , obtained in the form of its hydro-

chloride,  $C_{11}H_{11}O_2N \cdot HCl$ , deliquescent, white needles, m. p. 134–135°. The action of dilute hydrochloric acid on the corresponding nitrosamine (compare Gabriel, Abstr., 1905, i, 950), crystallises in regular prisms, m. p. 138°; the *platinichloride*,



forms brilliant, golden, rhombic crystals, m. p. 190° (decomp.). The ino-base decomposes when its aqueous solution is heated, with the formation of *β*-aminopropyl hydrogen phthalate,



crystallising in rhombic plates, m. p. 168° (decomp.); the *hydrochloride*,  $C_{11}H_{13}O_4N \cdot HCl \cdot 2H_2O$ , crystallises in pointed needles, melted partially at 87°, and is completely molten at 165°; the *platinichloride*,  $(C_{11}H_{13}O_4N)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , forms large, prismatic needles, m. p. 204° (decomp.). *β*-Hydroxypropylphthalimide,  $C_8H_8(CO)_2N \cdot C_3H_6 \cdot OH$ , reacts

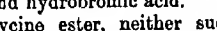
with *β*-bromopropylphthalimide is boiled with alcoholic potassium hydroxide; it crystallises in long prisms, m. p. 73°. *β*-Bromosuccinimide,  $C_4H_4O_2 \cdot N \cdot CH_2 \cdot CH_2Br$ , prepared by the action of ethylsuccinonitrile on sodium succinimide, forms white needles, m. p. 56–57°. It is converted by cold potassium hydroxide solution and subsequent treatment with hydrobromic acid into *β*-bromoethylsuccinamic acid,  $H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , crystallising in leaflets, m. p. 100°. This substance is very unstable, and does not give a nitrosamine when treated with potassium nitrite.

*γ*-Bromopropylsuccinimide,  $C_4H_4O_2 \cdot N \cdot C_3H_6Br$ , forms brilliant leaflets, m. p. 52°; the corresponding succinamic acid could not be obtained. An attempt to prepare *β*-bromopropylsuccinimide by the action of hydrogen bromide on allylsuccinimide was unsuccessful.

*γ*-Bromopropylidiphenylmaleinimide,  $\begin{matrix} CPh \cdot CO \\ CPh \cdot CO \end{matrix} > N \cdot C_3H_6Br$ , results

from the interaction of sodium diphenylmaleinimide and trimethylsuccinonitrile, crystallises in broad, yellow needles, m. p. 112°. *β*-Bromopropylidiphenylmaleinimide,  $C_{10}Ph_2 \cdot N \cdot C_3H_6Br$ , forms small, yellow crystals, m. p. 94°. These two derivatives of diphenylmaleinimide are more stable than the analogous phthalimide derivatives towards potassium hydroxide and hydrobromic acid.

Unlike phthalyl glycine ester, neither succinylglycine ester nor phenylmaleylglycine ester is converted by sodium ethoxide into a quinoline derivative. *Diphenylmaleylglycine ester*,



prepared by the action of ethyl chloroacetate on sodium diphenylmaleinimide, crystallises in yellowish-green needles, m. p. 109°. W. H. G.

**Intramolecular Condensation of Phthalanilic Acid and of Certain Allied Compounds. II.** J. BISHOP TINGLE and B. F. DELACROIX (*Amer. Chem. J.*, 1907, 38, 642–652).—Tingle and Delacroix (vol. i, 692) found that succinanilic acid readily combines

to aniline to form the anilide, whilst phthalanilic acid in presence of aniline and alcohol is converted into phthalanil even at the ordinary temperature. It is now shown that the latter change is due to the intermediate formation of aniline phthalanilate, which easily loses water and aniline with production of the anil. It has been found that pyridine and quinoline react with the acid in a similar manner to give a quantitative yield of the anil.

$\beta$ -Naphthylphthalamic acid reacts with aniline at  $100^\circ$  with formation of a mixture of phthalanil and  $\beta$ -naphthylphthalimide. Pyridine and quinoline under similar conditions give a quantitative yield of  $\beta$ -naphthylphthalimide. By the action of  $\beta$ -naphthylamine on the acid at  $100^\circ$ , a compound (probably di- $\beta$ -naphthylphthalamide), m. p.  $50^\circ$  (decomp.), is obtained. Benzylamine similarly yields *dibenzylphthalamide*,  $C_{20}H_{17}(CO \cdot NH \cdot CH_2Ph)_2$ , m. p.  $178-179^\circ$ .

When benzylphthalamic acid is heated with aniline at  $65^\circ$ , benzylphthalimide is produced together with a small quantity of a substance, m. p.  $177^\circ$ , which is probably dibenzylphthalamide. Pyridine and aniline react with the acid at  $100^\circ$  with formation of a quantitative yield of benzylphthalimide. Similarly,  $\beta$ -naphthylamine appears to give  $\beta$ -naphthylphthalimide. Benzylamine reacts with the acid at  $100^\circ$  with formation of dibenzylphthalamide. E. G.

**2:4(3:5-)Dihydroxytritanolactone and *m*-Hydroxytritanolactone.** HANS VON LIEBIG (*J. pr. Chem.*, 1907, [ii], 76, 367-368). The substance described as *m*-hydroxytritanolactone (this vol., i, 930) is now found to be identical with Baeyer and Diehl's *o*-hydroxytritanolactone (this vol., i, 759), and therefore is *o*-hydroxytritanolactone. It follows that the substance previously termed 3:5- is 2:4-dihydroxytritanolactone and that described as the 2:4- is the 2:6-dihydroxytritanolactone (Abstr., 1905, i, 781).

*o*-Hydroxytritanolactone is formed when *o*-methoxytritanolactone is boiled with concentrated hydriodic acid and glacial acetic acid. G. Y.

**Anomalies in the Condensation of Benzilic Acid with Homologues of Benzene.** AUGUSTIN BISTRZYCKI and LOUIS MAUBON (*Ber.*, 1907, 40, 4060-4065).—Benzilic acid in the presence of stannic chloride reacts in different ways with benzene and its monoalkyl homologues. Benzene and toluene yield the corresponding triarylated acetic acid, cumene reacts very slightly, the main product being diphenylacetic acid. This acid is also the main product of the reaction with ethylbenzene or propylbenzene in the presence of excess of benzene. *Diphenylacetic acid*,  $C_6H_5Et \cdot CPh_2 \cdot CO_2H$ , m. p.  $212-213^\circ$ , is obtained when benzilic acid, stannic chloride, and ethylbenzene are heated for two to three hours; it crystallises from dilute alcohol in aggregates of colourless leaflets, and loses carbon monoxide quantitatively by treatment with concentrated sulphuric acid (Abstr., 1904, 1915). *p*-Propyltriphenylacetic acid, m. p.  $256-257^\circ$ , behaves in a similar manner, forming *p*-propyltriphenylcarbinol, m. p.  $153-155^\circ$ . C. S.

**Preparation of Methyleneclitrylsalicylic Acid.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 185800).—*Methylene-*  
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*citrylsalicylic acid*,  $\text{CH}_2 \begin{smallmatrix} \text{O} \\ \diagup \text{CO}_2 \end{smallmatrix} \text{C}(\text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$ , colourless crystals, m. p. 150—155°, is obtained by condensing methylenecitryl chloride with salicylic acid in the presence of an agent for taking up hydrogen chloride, such as dimethylaniline or quinoline. It is also produced by digesting in benzene equivalent amounts of dipotassium salicylate and methylenecitryl chloride. It is more beneficial as an antirheumatic than acetylsalicylic acid, and has the additional property of yielding formaldehyde when hydrolysed by the alkaline intestinal juices. (G. T. M.)

**Preparation of *o*-Nitrobenzaldehyde.** ARNOLD REISSNER (D.R.-P. 186881. Compare this vol., i, 908).—The processes formerly employed to convert *o*-nitrotoluene into *o*-nitrobenzaldehyde either do not give a complete oxidation or lead to the formation of *o*-nitrobenzoic acid. It has now been found that the dimercury derivative of *o*-nitrotoluene (*loc. cit.*) is readily oxidised by dilute nitric or nitrous acid to *o*-nitrobenzaldehyde. To bring about this change, the dimercury compound is boiled with a 10% aqueous solution of potassium nitrate while 20% sulphuric acid is slowly added; the *o*-nitrobenzaldehyde is extracted with benzene or ether. A similar result is obtained with 20% nitric acid, or an aqueous solution of sodium nitrite, is added to a boiling mixture of 10% sulphuric acid and the dimercury compound. (G. T. M.)

***p*-Dimethylaminobenzaldehyde.** VI. FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, 40, 4356—4361. Compare, *Abstr.*, 1907, 2, 37; 1904, i, 506; 1905, i, 190, 202; 1906, i, 575).—It has been shown previously that, when magnesium methyl iodide and *p*-dimethylaminobenzaldehyde interact in the usual manner, the product is dimethylaminophenyl methyl carbinol,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{OH}$ . When, however, this product was heated at 100° with an excess of the Grignard reagent according to Klages' method, the corresponding unsaturated hydrocarbon,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CH}_2$ , was not formed, but in place of it, *p*-dimethylaminoisopropylbenzene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , was produced. That the latter compound has the constitution formerly assigned to it is, in the present paper, still further proved, since cumidine is formed from it by the elimination of two of the methyl groups by the method of von Braun.

*N*-Dimethylcumidine (*p*-dimethylaminoisopropylbenzene) was prepared as previously described; its *picrate* has m. p. 112°, and its *methiodide*, m. p. 165°.

*p*-isoPropylphenylmethylcyanamide,  $\text{CN} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , obtained by the action of cyanogen bromide on *N*-dimethylcumidine and subsequent elimination of methyl bromide, is a yellow oil, b. p. 165°/10 mm. When boiled with 30% sulphuric acid for ten minutes it forms *N*-methyl-*p*-isopropylaniline-*N*-carboxylamide,

$\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , which separates in rod-shaped crystals, m. p. 118°. When boiled for two to three hours with 30% sulphuric acid, the latter compound is converted into *N*-methylcumidine,  $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , which is

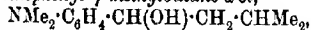
essence oil, b. p. 111—112°/11 mm.; its *hydrochloride* forms glistening crystals, m. p. 138°; its *platinichloride* has m. p. 193°; its *picrate* has m. p. 117°; its *benzoyl* derivative separates from light petroleum in needles, m. p. 58°. When acted on by phosphorus pentachloride, the *benzoyl* derivative is presumably first converted into the compound  $\text{PhCl} \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , from which methyl chloride is eliminated with formation of the imide chloride,  $\text{CPhCl} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ , which readily gives *N*-benzoylumidine,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}_2$ ; the latter compound crystallises from alcohol in glassy, spear-shaped crystals, m. p. 162°, and not 114° as given by Louis. The *N*-benzoylumidine obtained was hydrolysed by heating at 150° for twelve hours with concentrated hydrochloric acid, and the resulting benzoic acid and *lumidine* identified.

A. McK.

*p*-Dimethylaminobenzaldehyde. VII. FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, 40, 4361—4367. Compare preceding abstract).—When magnesium organic compounds react with *p*-dimethylaminobenzaldehyde, three different products may be obtained: (1) carbinols, according to the normal action; (2) unsaturated dicarbinols, when the carbinols are distilled under diminished pressure; (3) compounds, where the aldehydic oxygen atom is displaced by two alkyl groups. The method of conducting the latter change is as follows. The aldehyde (1 mol.) is gradually added to the cooled solution of magnesium alkyl bromide (4 mol.). After some time the ether is removed by heating the mixture, first on the water-bath, and finally under diminished pressure. The resulting grey, viscid mass is then heated in an oil-bath for about eight hours at 110°, and the product manipulated in the customary manner. The action of various magnesium organic compounds on *p*-dimethylaminobenzaldehyde is described in the present paper.

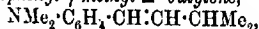
*p*-Dimethylaminophenylpropylcarbinol ( $\alpha$ -*p*-dimethylaminophenylcarbinol),  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Me}$ , obtained by the action of magnesium propyl bromide on *p*-dimethylaminobenzaldehyde under normal conditions, melts at 35°, but was not obtained quite pure, owing to its tendency to form the corresponding styrene derivative; the *methiodide* separates from a mixture of alcohol and ether in shining leaflets, m. p. 161°. When distilled under diminished pressure, the preceding secondary alcohol forms  $\alpha$ -*p*-dimethylaminophenyl- $\Delta^2$ -butylene,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{Me}$ , which boils at 116° under ordinary pressure, and has m. p. 25°; the *platinichloride* melts indefinitely at 140°; the *picrate* has m. p. 114·5°, and the *methiodide*, m. p. 212°.

$\alpha$ -*p*-Dimethylaminophenyl- $\gamma$ -methylbutane- $\alpha$ -ol,



obtained by the action of magnesium isobutyl bromide on *p*-dimethylaminobenzaldehyde, separates from light petroleum in stellate needles, m. p. 117°; its *methiodide* has m. p. 150°.

$\alpha$ -*p*-Dimethylaminophenyl- $\gamma$ -methyl- $\Delta^2$ -butylene,

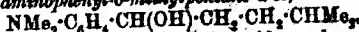


b. p. 148—149°/15 mm., is a liquid at the ordinary temperature, but



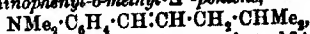
solidifies when immersed in a freezing mixture; its *picrate* has m. p. 137°, and its *platinichloride*, m. p. 154°.

*α-p-Dimethylaminophenyl-β-methylpentane-α-ol*,



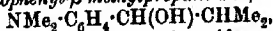
obtained from magnesium isosanyl bromide and *p*-dimethylaminobenzaldehyde, has m. p. 48°, and forms the *methiodide*, m. p. 141°.

*α-p-Dimethylaminophenyl-β-methyl-Δ<sup>α</sup>-pentene*,



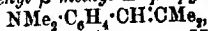
is a yellow oil at the ordinary temperature, b. p. 164–166°/0 mm., but solidifies when immersed in a freezing mixture; its *picrate* has m. p. 111°; its *platinichloride*, m. p. 167°, and its *methiodide*, m. p. 180°.

*α-p-Dimethylaminophenyl-β-methylpropane-α-ol*,



obtained from magnesium isopropyl bromide and *p*-dimethylaminobenzaldehyde, has m. p. 39°.

*α-p-Dimethylaminophenyl-β-methyl-Δ<sup>α</sup>-propylene*,



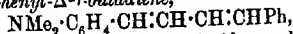
boils at 134–135°/11 mm., and has m. p. 37°; its *picrate* has m. p. 140°, and its *methiodide*, m. p. 170°.

*α-p-Dimethylaminophenyldiisopropylmethane* [*γ-p-dimethylaminophenyl-ββ-dimethylpentane*],  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CHMe}_2)_2$ , obtained from magnesium isopropyl bromide and *p*-dimethylaminobenzaldehyde, has m. p. 268°; its *picrate* has m. p. 150°, and its *methiodide* m. p. 171°.

*α-p-Dimethylaminophenyldiisoomylmethane* [*ε-p-dimethylaminophenyl-ββ-dimethylnonane*],  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe}_2)_2$ , obtained from magnesium isoomyl bromide and *p*-dimethylaminobenzaldehyde, is a colourless oil, b. p. 184–185°/13 mm.; its *methiodide* has m. p. 175°.

A. M. K.

**Action of Magnesium Organic Compounds on *p*-Dimethylaminocinnamaldehyde.** FRANZ SACHS and WALTER WEIGENT (*Ber.*, 1907, 40, 4368–4369. Compare preceding abstract).—The authors have studied the action of magnesium organic compounds on *p*-methylaminocinnamaldehyde. When magnesium ethyl bromide is used, the corresponding carbinol is not obtained, but the product when distilled under diminished pressure, gives *α-p-dimethylaminophenyl-Δ<sup>αγ</sup>-pentadiene*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CHMe}_2$ , which separates from alcohol in yellow crystals, m. p. 65°. Its solution in concentrated sulphuric acid is brown, and in dilute sulphuric acid red; its *picrate* has m. p. 145°. *γ-Phenyl-α-p-dimethylaminophenyl-Δ<sup>αγ</sup>-propene*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CHPh} \cdot \text{OH}$ , obtained from magnesium phenyl bromide and *p*-dimethylaminocinnamaldehyde, has m. p. 160° (decolor); its ethereal solution is yellow; its solution in glacial acetic acid is red; its solutions in chloroform and alcohol respectively brown. *β-Phenyl-α-p-dimethylaminophenyl-Δ<sup>αγ</sup>-butadiene*,



obtained from magnesium benzyl chloride and *p*-dimethylaminocinnamaldehyde, separates from light petroleum in yellow crystals, m. p. 171°.

A. M. K.

**Arylsulphonic Esters of Salicylaldehyde and its Homologues.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 183941).—The arylsulphonic esters of salicylaldehyde are produced by heating together at 70° an arylsulphonyl chloride and the aqueous solution of the sodium derivative of salicylaldehyde. The *p*-toluenesulphonyl derivatives of salicyl-, o-homosalicyl-, and *p*-homosalicylaldehydes are well-defined crystalline compounds melting respectively at 53–60°, 62°, and 68–69°. *Benzenesulphonyl-p-homosalicylaldehyde*, m. p. 63°, crystallises from petroleum in rectangular plates. When these arylsulphonyl derivatives are heated with the alkylbenzylsulphonic acids in the presence of aqueous acids, leucodisulphonic acids are produced, which, on oxidation with acetic acid and lead dioxide, give rise to coloured disulphonic acids of the malachite-green series. G. T. M.

**Preparation of 4-Benzoylaminoaceto-1:2-dialkyloxybenzenes.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 185598).—The action of hippuryl chloride on catechol leads to the attachment of the hippuryl group to one of the hydroxylic oxygens, with the formation of monohippuryl catechol. When this condensation is effected in the presence of aluminium chloride with a 1:2-dialkyloxybenzene instead of catechol, the hippuryl group enters the ring in the para-position to one of the oxygen atoms, so that compounds having the general formula  $C_6H_3(OR)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CPh$  are produced, these substances being utilised in the preparation of physiologically active compounds. 4-Benzoylaminoacetylveratrole,  $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CPh$ , melted needles, m. p. 155°, and 4-benzoylaminoacetyl-1:2-diethoxybenzene,  $C_6H_3(OEt)_2 \cdot CO \cdot CH_2 \cdot NH \cdot CPh$ , needles, m. p. 162°, are thus obtained from veratrole and 1:2-diethoxybenzene respectively. G. T. M.

**Hexahydroacetophenone, Dodecahydrobenzophenone, Dodecahydridiphenyl, and other Hydroaromatic Derivatives.** CARL HELL and OSCAR SCHAAL (*Ber.*, 4162–4166. Compare von Braun, *ibid.* vol. i, 893).—The best method of preparation of cyclohexyl methyl ketone is from cyclohexanol by first preparing cycloiodohexane, then causing the magnesium cyclohexyl iodide to condense with acetyl chloride, and oxidising the secondary alcohol so obtained to the ketone. The yield is 50% of the cyclohexanol employed. Contrary to von Braun's statement, this ketone gives a hydrogen sulphite compound. Cyclohexyl methyl ketone is also obtained in small yield by the distillation of a mixture of barium cyclohexanecarboxylate and acetate; acetone, and dicyclohexyl ketone,  $CO(C_6H_{11})_2$ , an oily liquid, b. p. 131–161°/14 mm., are also formed. Attempts to prepare cyclohexyl methyl ketone by reducing acetophenone by sodium and amyl alcohol, by the condensation of acetyl chloride and cyclohexanol, and by the interaction of acetonitrile and magnesium cyclohexyl iodide were without result.

The yield of iodocyclohexane from cyclohexanol is quantitative, whereas that of the bromo- and chloro-derivatives is only 50% (compare Fremder and Dammond, *Abstr.*, 1905, i, 890).

All three haloid compounds give by the Grignard reaction a normal organomagnesium compound, *cyclohexene*, and, in addition, the iodide yields *dodecahydrodiphenyl* [dicyclohexyl],  $C_6H_{11} \cdot C_6H_{11}$ , an agreeable-smelling liquid, m. p.  $4^\circ$ , b. p.  $234^\circ/760$  mm. A cryoscopic determination shows the mol. wt. to be 164, calc. 166; it reacts in sunlight very energetically with bromine.

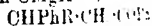
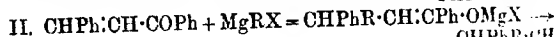
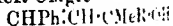
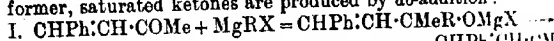
Magnesium methyl iodide and ethyl *cyclohexanecarboxylate* give *cyclohexyldimethylcarbinol*, b. p.  $85-86^\circ/14$  mm. (compare Salasier and Mailhe, Abstr., 1904, i, 810); the corresponding *diethyl* compound,  $C_6H_{11} \cdot C_2H_5 \cdot OH$ , has b. p.  $104-106^\circ/14$  mm. The *diphenyl* compound is an oily liquid, which loses water at  $210-220^\circ/14$  mm., and by several distillations the unsaturated *hydrocarbon*,  $C_6H_{10} \cdot C_6H_5$ , is obtained, crystallising from methyl alcohol in prisms, m. p.  $84^\circ$ . W. R.

**Halogen Derivatives of Benzophenone and of Di- and Tri-phenylmethane.** FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1907, 44, 50-60).—Determinations of the crystalline forms of the following compounds: 2-bromobenzophenone; 2:4'-dichlorobenzophenone; 2:4:6-trichlorobenzophenone; 4:4'-dichlorodiphenylmethane;  $\alpha$ :4:4'-trichlorodiphenylmethane;  $\alpha$ -bromodiphenylmethane; phenylindoxazen; 4:4':4''-tribromotriphenylmethane; 4:4':4''-trinitrotriphenylcarbinol; reduction product from 4:4':4''-tetrachlorobenzopinacolin; 4:4':4''-tetrachlorotetraphenylethane.

L. J. S.

### Reaction Between Unsaturated Compounds and Organic Magnesium Compounds. XII. Aldehydes and Ketones

ELMER P. KOHLER (*Amer. Chem. J.*, 1907, 38, 511-561).—In an earlier paper (Abstr., 1904, i, 595), an account was given of the action of organic magnesium compounds on  $\alpha\beta$ -unsaturated ketones containing phenyl in combination with the carbonyl group. On comparing the reactions of these phenyl ketones with those of corresponding methyl ketones, it has been observed that in the latter  $\alpha\beta$ -addition takes place with formation of unsaturated alcohols, whilst, in the former, saturated ketones are produced by  $\alpha\delta$ -addition:



An investigation has been made with the object of ascertaining whether all unsaturated ketones behave in one or other of these ways, or whether substances could be found which would give both reactions. It has been found that certain ketones react in both ways, but that the relative proportions in which the  $\alpha\beta$ - and  $\alpha\delta$ -addition takes place depend on the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues and the character of the magnesium derivative. Experiments have been made to determine the relative importance of these factors, and attempts have been made to estimate the amounts of the various products.

In carrying out the experiments, the unsaturated compound was added gradually to a large excess of the reagent, cooled in a freezing mixture. The product was poured on ice and treated with alkali.

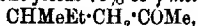
acetic acid to remove basic salts. The ethereal layer was separated, dried, and distilled; the residue was dissolved in acetone and treated with powdered potassium permanganate, the temperature being kept below 20°. In this way, the unsaturated products were destroyed and the saturated ketone could be collected and weighed. The quantitative results are expressed as the percentage of the unsaturated compound represented by the amount of  $\alpha\beta$ -additive product obtained. Most ketones yield both unsaturated alcohols and saturated ketones, whilst aldehydes yield the former only.

It is shown that the activity of the carbonyl group in unsaturated ketones varies in the same way as that of the corresponding saturated compounds, and that it merely determines the rate of the reaction. The final result depends quite as much on the rate of  $\alpha\delta$ -addition, and substances in which the activity of the carbonyl group is approximately the same may give almost entirely different products with the same reagent. The reactivity of the unsaturated compounds undergoes a gradual diminution as the hydrogen atoms are successively replaced by hydrocarbon residues, and the phenomena observed can be satisfactorily explained as being due to steric hindrance. The effect produced on the reaction by the nature of the magnesium derivative is shown by the different relative amounts of  $\alpha\beta$ - and  $\alpha\delta$ -additive products obtained with magnesium ethyl and magnesium phenyl bromides. Variations in the temperature and solvent do not appreciably affect the result.

The behaviour of unsaturated compounds resembles that of aromatic substances, but in the case of the unsaturated ketones the results cannot be explained by intermediate compounds or by assuming that only one of the products is formed directly. In this case, the two additive reactions are so independent of each other that their rates are governed by quite different factors. The only satisfactory explanation therefore is that these unsaturated compounds can exist in two modifications, such as  $C:C:C:C$  and  $-C:C:C-C-$ .

By the action of magnesium ethyl bromide on acetaldehyde, ethyl-ethylcarbinol is produced, whilst with magnesium phenyl bromide, phenyl-ethyl alcohol is formed.

Ethylideneacetone reacts with magnesium methyl bromide with formation of dimethylisobutylcarbinol and methyl isobutyl ketone, the latter forming about 75% of the product. With magnesium ethyl bromide, ethylideneacetone yields 75% of  $\gamma$ -methylhexane- $\epsilon$ -one,



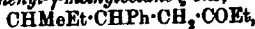
b. p. 146°–147°, whilst with magnesium phenyl bromide it gives 40% of 3-phenylpropyl methyl ketone,  $CHPhMe \cdot CH_2 \cdot COMe$ , b. p. 132°/22 mm., which furnishes an oxime, b. p. 160°/22 mm., as a viscous liquid.

In the case of mesityl oxide,  $\alpha\delta$ -addition does not take place.

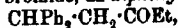
Benzylideneacetone (styryl methyl ketone) reacts with magnesium ethyl bromide or iodide with production of 60% of phenylhexanone,  $CHPhEt \cdot CH_2 \cdot COMe$ , b. p. 130°/18 mm., which yields an oxime, b. p. 170°/20 mm. With magnesium phenyl bromide, it gives 12% of  $\delta$ -diphenylethyl methyl ketone,  $CHPh_2 \cdot CH_2 \cdot COMe$ , b. p. 194°/20 mm.

(compare Abstr., 1904, i, 596). The *ketoisomer* exists in two forms, m. p. 91° (plates) and 128° (needles).

Styryl ethyl ketone, on treatment with magnesium ethyl bromide yields 71% of  $\gamma$ -phenylheptanone,  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{COEt}$ , b. p. 255°, which gives an *oxime*, b. p. 172°/18 mm. With magnesium isobutyl bromide a similar yield of  $\delta$ -phenyl- $\gamma$ -methyloctane- $\epsilon$ -one,

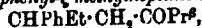


b. p. 152°/17 mm., is obtained, which furnishes an *oxime*, b. p. 188°. With magnesium phenyl bromide, *aa*-diphenylpentane- $\gamma$ -one,

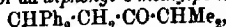


b. p. 334—335°, is produced in a yield of 40% of the unsaturated ketone; its *oxime* exists in two stereoisomeric modifications, m. p. 146° (needles) and 117° (plates).

Styryl isopropyl ketone reacts with magnesium ethyl bromide with formation of 100% of  $\gamma$ -phenyl- $\zeta$ -methylheptane- $\epsilon$ -one,

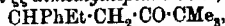


b. p. 138°/15 mm.; the *oxime* has b. p. 175°/18 mm. With magnesium phenyl bromide, 88% of *aa*-diphenyl- $\delta$ -methylpentane- $\gamma$ -one,

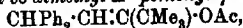


m. p. 66°, is produced, which forms colourless prisms and yields two isomeric *oximes*, m. p. 151° (needles) and 99° (plates); the  $\beta$ -bromo derivative,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{Pr}^i$ , m. p. 108°, crystallises in needles, and is converted by potassium hydroxide into *aa*-diphenyl- $\delta$ -methyl- $\Delta^2$ -pentene- $\gamma$ -one,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CHMe}_2$ , b. p. 210—211°/15 mm.

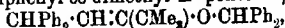
Benzylidenepinacolone, on treatment with magnesium ethyl bromide, yields 100% of  $\gamma$ -phenyl- $\zeta$ -dimethylheptane- $\epsilon$ -one,



b. p. 145°/15 mm., m. p. 34°, which crystallises in needles, and yields a mixture of *oximes*, m. p. 83° (needles) and 36° (prisms). With magnesium phenyl bromide, 100% of *aa*-diphenyl- $\delta\delta$ -dimethylpentane- $\gamma$ -one,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}_2$ , m. p. 85°, is obtained, and forms slender needles. If acetyl chloride is added to the magnesium compound produced by the action of magnesium phenyl bromide on benzylidenepinacolone, *aa*-diphenyl- $\delta\delta$ -dimethyl- $\Delta^2$ -pentenyl  $\gamma$ -acetate,

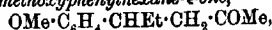


m. p. 165°, is obtained, and crystallises in brilliant plates. The magnesium compound does not react with simple alkyl halides, but reacts with diphenylbromomethane with formation of the diphenylmethyl ether of *aa*-diphenyl- $\delta\delta$ -dimethyl- $\Delta^2$ -pentene- $\gamma$ -ol,



m. p. 224°, which crystallises in plates.  $\beta$ -Bromo-*aa*-diphenyl- $\delta\delta$ -dimethylpentane- $\gamma$ -one,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CMe}_2$ , m. p. 145°, crystallises in plates, and is converted by potassium hydroxide into *aa*-diphenyl- $\delta\delta$ -dimethyl- $\Delta^2$ -pentene- $\gamma$ -one,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}_2$ , m. p. 112°, which forms pale yellow plates.

*p*-Methoxybenzylideneacetone reacts with magnesium ethyl bromide to form 63% of  $\gamma$ -*p*-methoxyphenylhexane- $\epsilon$ -one,



b. p. 170°/18 mm., which yields an *oxime*, b. p. 195°/18 mm.

Dibenzylideneacetone and magnesium ethyl bromide react with formation of 91% of benzylidenephénylhexanone [*aa*-diphenyl- $\Delta^2$ -hexanone]

$\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPhEt}$ , b. p. 224–228°, m. p. 87°, which forms long needles; the *oxime*, m. p. 117°, crystallises in needles. With magnesium phenyl bromide, 73% of *benzylidenediphenylbutanone* [ $\alpha$ -*triphenyl- $\Delta^4$ -pentanone*],  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , m. p. 136°, is produced, which forms pale yellow needles, and yields an *oxime*, m. p. 144°, which crystallises in needles. By the action of bromine on the preceding compound,  $\alpha\beta$ -*dibromo- $\alpha$ -triphenylpentanone- $\gamma$ -one*,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , obtained, and forms colourless needles.

Diphenylheptenone reacts with magnesium ethyl bromide to form 93% of  $\gamma\gamma$ -*diphenylnonanone- $\epsilon$ -one*,  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPhEt}$ , m. p. 56°, which crystallises in needles. With magnesium phenyl bromide, 93% of *alpha-triphenylheptanone- $\gamma$ -one*,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPhEt}$ , p. 72°, is produced together with about 7% of an unsaturated compound formed by  $\alpha\beta$ -addition; the *bromo-derivative*,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPhEt}$ , p. 155°, crystallises in needles.

Triphenylpentanone and magnesium ethyl bromide yield 100% of phenylheptanone. With magnesium phenyl bromide, 99% of tetra-*acetyl*pentanone is produced together with a very small proportion of saturated compounds formed by  $\alpha\beta$ -addition.  $\beta$ -*Bromo- $\alpha$ -acetyl- $\alpha$ -triphenylpentanone- $\gamma$ -one*,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ , m. p. 160°, crystallises in needles. Trichloroethylideneacetophenone reacts with magnesium phenyl bromide with formation of 95% of *alpha-trichloro- $\beta$ -phenylbutyrophenone*,  $\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ , m. p. 137°. Benzylidenacetophenone and magnesium ethyl bromide yield 99% of *phenylvalerophenone* [ $\gamma$ -*diphenylpentanone- $\epsilon$ -one*],  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{COPh}$ , p. 63°, which forms thin needles and gives an *oxime*, m. p. 87°. With magnesium phenyl bromide, 94% of diphenylpropionphenone is obtained.

Anisylidenacetophenone and magnesium ethyl bromide react with formation of 98% of *p-methoxyphenylvalerophenone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{COPh}$ , p. 58°, which crystallises in thick, lustrous needles; the *oxime*, p. 92°, forms prisms. With magnesium phenyl bromide, 96% of *isopropenylpropionphenone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$ , m. p. 93°, is obtained and forms stout needles.

Anisyl styryl ketone and magnesium ethyl bromide yield 100% of *benzylbutyl anisyl ketone*,  $\text{CHPhEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Me}$ , m. p. 85°, which crystallises in long, thin needles, and furnishes an *oxime*, p. 72°. With magnesium phenyl bromide, 99% of *diphenylethyl val ketone*,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 118°, is produced; its *oxo-derivative*, m. p. 144°, is converted by potassium hydroxide to  *$\beta$ -phenylstyryl anisyl ketone*,  $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 103°, which yields a *bromo-derivative*,  $\text{CPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 71°.

Cinnamoylmesitylene,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , m. p. 63°, prepared by adding aluminium chloride to a solution of mesitylene and

cinnamoyl chloride in carbon disulphide, forms large, yellow plates, and is converted by bromine into  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionylmesitylene,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Me}_3$ , m. p.  $122^\circ$  (decomposes); it reacts with magnesium phenyl bromide with formation of 100% of  $\beta\beta$ -diphenylpropionylmesitylene,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Me}_3$ , which yields a bromo-derivative,  $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Me}_3$ , m. p.  $115^\circ$ . When the bromo-derivative is treated with potassium hydroxide, it is converted into phenylcinnamoylmesitylene,  $\text{CHPh}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Me}_3$ , m. p.  $104^\circ$ , which forms dark yellow plates.

By the reactions of bromobenzylideneacetophenone, benzylidenepropionophenone, and benzylidenedecybenzoin with magnesium alkyl halides, unsaturated compounds formed by  $\alpha\beta$ -addition are not produced, and it is evident therefore that substituents in the  $\alpha$ -position interfere with the addition to the carbonyl group.

Dypnone reacts with magnesium ethyl bromide with formation of 44% of  $\beta$ -phenyl- $\beta$ -methylvalerophenone,  $\text{CPhMeEt}\cdot\text{CH}_2\cdot\text{COPh}$ , b. p.  $202^\circ/18$  mm.; its oxime, b. p.  $222^\circ/15$  mm., is amorphous. The quantity of diphenylbutyrophenone formed by the action of magnesium phenyl bromide on dypnone (Abstr., 1904, i, 596) is 41%.

Phenylbenzylideneacetophenone and magnesium ethyl bromide yield 18% of  $\beta\beta$ -diphenylvalerophenone,  $\text{CHPh}_2\text{Et}\cdot\text{CH}_2\cdot\text{COPh}$ , b. p.  $252^\circ/15$  mm.; its oxime was prepared. With magnesium phenyl bromide, a saturated ketone is not produced, but the unsaturated alcohol and hydrocarbon are obtained, which have been described by Vorländer, Siebert, and Osterburg (Abstr., 1906, i, 346).

Diphenylbenzylideneacetophenone,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{COPh}$ , m. p.  $137^\circ$ , obtained by the action of potassium hydroxide on bromotriphenylpropionophenone, forms pale yellow needles and is very inactive. When treated with magnesium ethyl bromide, an unsaturated hydrocarbon is produced, and indications are obtained of the formation of a saturated ketone.

Magnesium phenyl bromide reacts with benzoylphenylacetylene with formation of hydroxytriphenylpropinene (benzophenonephenylacetylene) (Nef, Abstr., 1900, i, 21), but a saturated ketone is not produced.

E. G.

**Derivatives of Fluorenoneoxime.** Contribution II. to the Theory of Colour. JULIUS SCHMIDT and JULIUS SÖLL (Ber., 1907, 40, 4257—4260. Compare this vol., i, 630).—The authors have prepared fluorenone and its oxime and various derivatives of the latter, and have repeatedly crystallised them from suitable solvents until their colours underwent no further change. Thus purified fluorenone is reddish-yellow; fluorenoneoxime, bright yellow; its sodium salt, pale yellow; its acetyl and benzoyl derivatives, bright yellow; and its methyl ether, reddish-yellow. As with phenanthrenequinone, so also with fluorenone, replacement of the ketonic oxygen by the hydroxyimino-group is accompanied by brightening of the colour. Not so distinct, but still appreciable, is the effect which the introduction of acetyl, benzoyl, or sodium into the molecule of fluorenoneoxime has in brightening the colour.

*Fluorenoneoxime methyl ether*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{N} \end{smallmatrix} \text{OMe}$ , crystallises from benzene in reddish-yellow needles, m. p. 145–146°, and dissolves easily in all the ordinary solvents except light petroleum. The acetyl derivative of fluorenoneoxime has m. p. 79°; Wegerhoff (Ann., 1888, 252, 36; Abstr., 1889, 1066) gave 76°. These derivatives of fluorenoneoxime are dissolved by concentrated sulphuric acid, giving reddish-brown solutions, from which they are reprecipitated by the addition of water. T. H. P.

**Constitution and Colour of Derivatives of *o*-Benzoquinone- and Naphthaquinone-dioximes.** ARTHUR HANTZSCH and WALTER F. GLAUBER (Ber., 1907, 40, 4344–4350. Compare this vol., i, 101).—Faint *o*-benzoquinonedioxime is faintly coloured, it forms dark red salts and also a colourless anhydride. It could not be determined whether the alkyl (or acyl) derivatives of the type  $\text{OR} \cdot \text{N} : \text{C}_6\text{H}_4 : \text{N} \cdot \text{OR}$  are colourless, since the salts are so readily transformed into the anhydrides, thus:  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{ONa} \\ \diagdown \diagup \\ \text{N} \cdot \text{OH} \end{smallmatrix} = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagdown \diagup \\ \text{N} \end{smallmatrix} \text{O} + \text{NaOH}$ . Analogous derivatives of  $\beta$ -naphthaquinonedioxime,  $\text{OR} \cdot \text{N} : \text{C}_{10}\text{H}_6 : \text{N} \cdot \text{OR}$ , are colourless, in spite of the fact that the anhydride,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagdown \diagup \\ \text{N} \end{smallmatrix} \text{O}$ , is colour-

less. The intensity of the colour of these compounds depends largely on the solvent. The dioxime salts of the benzene series are red, those of the phenanthrene series yellow; the alkyl and acyl derivatives of the naphthalene series are yellow, those of the phenanthrene series are colourless. The intensity of colour during salt formation from derivatives of *o*-benzoquinonedioxime indicates that the latter are *pseudo*-acids.

Aqueous solutions of *o*-benzoquinonedioxime are yellow and faintly acid in reaction. Determinations of electrical conductivity showed that *o*-benzoquinonedioxime is 100 times as weak as acetic acid. The solutions of the dioxime in alkalis are blood-red; the salts are, however, very unstable, and from their aqueous solutions the colourless anhydride separates. When dry ammonia is passed into the yellow solution of the dioxime in absolute ether, there is no precipitate, and the colour does not change. The solutions of the dioxime in strong acids are also blood-red. Tetrabromo-*o*-benzoquinonedioxime benzyl ether was not formed from benzyl hydroxylamine and tetrabromo-*o*-benzoquinone; in place of it, *benzylhydroxylaminotribromo-o-quinone*,  $\text{C}_6\text{Br}_3\text{O}_2 \cdot \text{NH} \cdot \text{O} \cdot \text{C}_7\text{H}_7$ , was produced; it separates from glacial acetic acid or benzene in orange-coloured needles, m. p. 170° (decomp.).

Various salts of  $\beta$ -naphthaquinonedioxime  $\alpha$ -methyl ether were prepared, namely, the normal potassium salt, hydrogen potassium salt, and the silver salt. The benzoyl derivative,  $\text{OMe} \cdot \text{N} : \text{C}_{10}\text{H}_6 : \text{N} \cdot \text{OBz}$ , has m. p. 116–119°; the yellow tint of the benzoyl derivative in various solvents is not so pronounced as that of the parent substance.

*$\beta$ -Naphthaquinonedioxime  $\alpha$ -benzyl ether*,  $\text{OH} \cdot \text{N} : \text{C}_{10}\text{H}_6 : \text{N} \cdot \text{O} \cdot \text{C}_7\text{H}_7$ , obtained by the action of hydroxylamine on benzyl ether monoxime,



separates from a mixture of chloroform and acetone in yellow prisms, m. p.  $168^{\circ}$ ; its *benzoyl* derivative forms needles, m. p.  $169^{\circ}$ . The colour of these compounds in various solvents was studied.

A. McK.

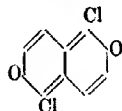
**Quinonoid Compounds. XIV. *amphiNaphthaquinones*.** RICHARD WILLSTÄTTER and JAKOB PARNAS (*Ber.*, 1907, 40, 3971—3979. Compare this vol., i, 425).—An account of the formation of 1:5-dichloro*amphinaphthaquinone* and its derivatives.

1:5-Dichloro-2:6-dihydroxynaphthalene,  $C_{10}H_6O_2Cl_2$ , prepared by the action of chlorine on 2:6-dihydroxynaphthalene in glacial acetic acid solution, crystallises in needles containing  $2C_2H_5O_2$ , lost on exposure to air, or from benzene in hexagonal plates, m. p.  $223.5^{\circ}$  (corr.). It forms a diacetate,  $C_{12}H_{10}O_4Cl_2$ , crystallising in plates, m. p.  $172^{\circ}$  (corr.).

1:5-Dichloro*amphinaphthaquinone* (annexed formula), obtained in a 36—45% yield by oxidation of the 2:6-dihydroxy-compound with lead dioxide in benzene solution, crystallises from chloroform in reddish-yellow prisms, or from alcohol in golden needles, or from benzene-light petroleum in brownish-yellow needles, m. p.  $206.5^{\circ}$  (corr.) (intumesces), is not volatile, odourless, stable in air, and more stable than *amphinaphthaquinone* towards organic solvents; it dis-

solves only slowly in alkalis, gives an olive-green coloration with concentrated sulphuric acid, and is reduced to 1:5-dichloro-2:6-dihydroxynaphthalene by sulphurous acid, dilute hydriodic acid, or phenylhydrazine in benzene solution. The dichloro*amphinaphthaquinone* is an energetic oxidising agent; it gives a blue coloration with guaiacum resin solution, converts hydrocoerulignone into coerulignone, and forms malachite-green from the *leuco*-base. It yields a colourless, crystalline acetate with acetic anhydride in presence of sulphuric acid, and combines with 2:6-dihydroxy- and 1:5-dichloro-2:6-dihydroxynaphthalenes, forming *amphinaphthaquinonehydrones*, crystallising in dark green needles, and giving an intense emerald-green coloration with concentrated sulphuric acid.

The action of *as*-benzoylphenylhydrazine on 1:5-dichloro*amphinaphthaquinone* in glacial acetic solution leads to the formation of the *a*-benzoylphenylhydrazone of 5-chloro-6-hydroxy- $\beta$ -naphthaquinone,  $C_{23}H_{15}O_3N_2Cl$ , which crystallises in yellowish-red plates or red prisms, m. p.  $224^{\circ}$  (corr.), is extracted unchanged from its ethereal solution by dilute potassium hydroxide, is stable towards phenylhydrazine in boiling benzene solution, and forms a brilliant reddish-yellow solution in alcohol which is decolorised by zinc dust and acetic acid. When treated with concentrated sulphuric acid, the benzoylhydrazone is hydrolysed, forming the *a*-phenylhydrazone,  $C_{18}H_{11}O_3N_2Cl$ , which crystallises from glacial acetic acid in yellowish-red needles, m. p.  $198^{\circ}$  (corr.), and dissolves in aqueous alkalis forming intense brownish-red, or in very dilute solutions in bluish-red, solutions. The phenylhydrazone and benzoylphenylhydrazone on treatment with benzoyl chloride in pyridine solution yield the *di*benzoyl derivative,  $C_{30}H_{19}O_4N_2Cl$ , which crystallises in brownish-yellow prisms, m. p.  $208.5^{\circ}$  (corr.), gives a cherry-red color-



a with concentrated sulphuric acid, and forms benzanilide on reduction;  
 b with zinc dust and acetic acid. G. Y.

**Preparation of Leucohydroxyanthraquinone.** FARBERKE FORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 183332).—Leucoquinizarin produced from 2:4-dinitro-1-anthraquinone by reducing this to the corresponding diamino-compound with stannous chloride and then heating the mixture for eight hours; the leuco-base separates on cooling. A similar result is obtained on reducing 2:4-dinitro-1-hydroxyanthraquinone with sodium sulphide and then boiling the 2:4-diamino-1-hydroxyanthraquinone thus produced with stannous chloride and hydrochloric acid.

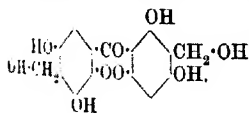
The reduction of the dinitrohydroxyanthraquinones containing one nitro group in the ortho- and one in the para-position to the hydroxy-group leads to the same result as the reduction of the mono-nitro-compounds, but, as the polynitro-derivatives are more readily obtained, there is a technical advantage in starting with the more highly nitrated products. G. T. M.

**Preparation of Alkylated 4:8-Diaminoanthrarufins.** FARBERKE FORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 185546).—Alkylated 4:8-diaminoanthrarufins are obtained by treating the 4:8-halogen derivatives of anthrarufin with the monoalkylamines in the presence of a catalyst, such as copper. The products when sulphonated furnished soluble wool dyes.

4:8-Diethyl-4:8-diaminoanthrarufin, bronze needles, m. p. 292°, and 4:8-dimethyl-4:8-diaminoanthrarufin, dark blue needles, m. p. above 300°, were prepared by heating at 100° in the presence of copper powder 4:8-diaminoanthrarufin and 20% alcoholic solutions of ethylamine and methylamine respectively. G. T. M.

**Preparation of 1:2:5-Trihydroxyanthraquinone and 1:2:5-Trihydroxyanthraquinone-3-sulphonic Acid.** FARBENFABRIKEN AG. FRIEDR. BAYER & Co. (D.R.-P. 178631).—1:2:5-Trihydroxyanthraquinone is obtained readily by heating 5 parts of sodium alizarin-sulphonate with 15 parts of sodium hydroxide and 3 parts of water at 180–200°, and then acidifying the aqueous extract of the fused mass. The trihydroxy-compound is deposited in yellow flakes. The acid fusion of sodium 1:2:5-trihydroxyanthraquinone-3-sulphonic acid, which separates in yellow flakes, soluble in water, and reprecipitated by cooling out. G. T. M.

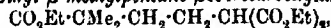
**Preparation of  $\omega$ -Dihydroxydimethyl-2:6-anthrachrysone.** FARBERKE FORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 184768).—Anthrachrysone readily reacts with formaldehyde in alkaline solution to yield an insoluble yellow condensation product, which is probably  $\omega$ -dihydroxy-



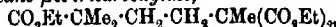
*oxydimethyl-2:6-anthrachryson*. The sodium salt is a well defined sparingly soluble compound, separating in garnet-red crystals.

G. I. M.

**Syntheses in the Camphor Group. Complete Synthesis of Campholene.** GUSTAVE BLANC (*Compt. rend.*, 1907, 145, 681).—The author has synthesised campholene by a similar method to that employed in the synthesis of its lower homologue, isolaurelene (Abstr. 1906, i, 523). *Ethyl β-methylpentane-β-tricarboxylate*,



obtained by the condensation of ethyl γ-bromo-αα-dimethylbutyrate with ethyl sodiomalonate, is a colourless liquid, b. p. 175°/12 mm., and reacts with methyl iodide in the presence of sodium ethoxide to yield *ethyl β-methylhexane-β-tricarboxylate*,



b. p. 168°/14 mm.; the corresponding acid forms sparingly soluble white needles, melts at 205°, losing carbon dioxide and forming ααδ-trimethyladipic acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , m. p. 113—114°, which is probably identical with the acid obtained by Wallach and Kempe in the oxidation of pulenone (Abstr., 1904, i, 114). ααδ-Trimethyladipic anhydride is converted by careful distillation into

1:1:4-trimethylcyclopentane-5-one,  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad \quad | \\ \text{CHMe} \cdot \text{CO} \end{array} > \text{CMe}_2$ , b. p. 152°/12 mm.

liquid having an odour similar to that of camphor or menthone; it forms an oxime, m. p. 62°, and condenses with magnesium and

iodide to form the tertiary alcohol,  $\begin{array}{c} \text{CH}_2 - \text{CMe}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CHMe} \end{array} > \text{CMe} \cdot \text{OH}$ , an oil

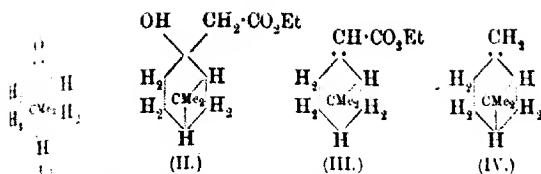
liquid, b. p. 72°/18 mm., having an intense musty, camphoraceous odour, which yields campholene,  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad \quad | \\ \text{CMe} \cdot \text{CMe} \end{array} > \text{CMe}_2$ , on distillation

under ordinary pressure.

M. A. W.

**Terpenes and Ethereal Oils. LXXXVIII.** OTTO WALLACH (*Annalen*, 1907, 367, 49—71).—I. *Synthesis from Nopinone of a Hydrocarbon related to β-Pinene*.—β-Pinene (nopinene) occurs commonly in small amounts in various turpentine oils, but, as it has not yet been isolated from these, its physical and other properties are not definitely known. It seemed therefore of interest to synthesise a hydrocarbon having the structure of β-pinene. Starting from nopinone (Wallach and Blumann, this vol., i, 936), this has now been accomplished by the method previously employed (Abstr., 1906, i, 563) for the introduction of a methylene group into cyclic hydrocarbons.

The action of zinc and ethyl bromoacetate on nopinone (I) in benzene solution leads to the formation of the *hydroxy-ester* (II), which has not been isolated, but when heated, after removal of the benzene, with potassium hydrogen sulphate at 150° yields the unsaturated ester (III). On hydrolysis of this, the acid is obtained as a syrup, b. p. 190—210°/13 mm.; the silver salt,  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{Ag}$ , was analysed. When distilled under atmospheric pressure, the acid loses carbon dioxide and forms a β-pinene (IV), b. p. 158°,  $D_4^{20}$  0.8630,  $[\alpha]_D^{20} + 15.93^\circ$  undiluted or  $+ 12.76^\circ$  in ethereal solution,  $n_D^{20}$  1.4699:



On oxidation with potassium permanganate and sodium hydroxide at 100°C. the hydrocarbon yields a sparingly soluble *sodium* salt, which resembles sodium nopalate obtained from turpentine oil, but is dextrorotatory; the *cr* salt,  $C_{10}H_{15}O_3Ag$ , was analysed. The *acid* crystallises from benzene needles, m. p.  $154-155^\circ$ , is dextrorotatory, and differs from nopic acid in recrystallising unchanged from dilute sulphuric acid. The mother liquors from the acid contain small amounts of a substance, m. p.  $110-122^\circ$ . Oxidation of the acid with permanganate leads to the formation of a *ketone*,  $C_9H_{14}O$ , m. p. about  $60^\circ$ , which is a *semicarbazone*,  $C_{10}H_{17}ON_2$ , m. p.  $206-207^\circ$ .

The action of hydrogen chloride on the hydrocarbon leads to the formation of liquid *additive* compounds, whilst that of sulphuric acid leads to the formation of a crystalline, saturated, secondary *alcohol*,  $C_{10}H_{18}O$ , which has an odour of camphor, and on oxidation with chromic acid yields a *ketone*,  $C_{10}H_{16}O$ . This solidifies below  $0^\circ$ , has an odour of camphor and menthone, and forms a *semicarbazone*,  $C_{11}H_{18}ON_2$ , crystallising in needles, m. p.  $220-221^\circ$  (compare Aschan, this vol., p. 600).

The relation of the synthetical  $\beta$ -pinene to that occurring in turpentine oil is discussed; it is considered that a change in the configuration takes place during the conversion of the nopinone into a synthetical hydrocarbon. Of special interest is the formation of a secondary alcohol from a hydrocarbon containing the grouping:



II. *Synthesis of Homologous Compounds of the Dipentene Series.*—It has been shown (Wallach and Blumann, *loc. cit.*) that methylpinol is readily converted, on the one hand, into terpin hydrate and pinene, and, on the other, into terpinolene and terpinene. Probably similarly active limonene and  $\alpha$ -pinene also are formed. These reactions have now been employed in the formation of homologues of the terpene derivatives.

*Ethylnopinol*,  $C_{11}H_{20}O$ , prepared by the action of magnesium ethyl chloride on nopiunone, forms large crystals, m. p.  $43-45^\circ$ , b. p.  $219-223^\circ$ , when heated with formic acid loses water and yields homologous terpenes. When shaken with 5% sulphuric acid, ethylnopinol yields a *homologue* of terpin hydrate having the annexed constitution, which forms transparent crystals containing  $H_2O$ , m. p.  $75-76^\circ$ , and is readily converted into the *dihydrochloride*,  $C_{11}H_{18}2HCl$ , m. p.  $63-64^\circ$ . This is formed also by the action of hydrogen chloride on ethylnopinol in glacial acetic acid solution, and closely resembles

dipentene dihydrochloride. The *dihydrobromide*,  $C_{11}H_{18} \cdot 2HBr$ , m. p. 82—84°; the *dihydriodide*, m. p. 63—64°.

The *hydrocarbon*,  $C_{11}H_{18}$ , b. p. 201—202°, prepared by treating the dihydrochloride with aniline, yields a crystalline *bromide*,  $C_{11}H_{18}Br_2$ , m. p. 124—125°, and a crystalline *nitrosobromide*, which loses hydrogen chloride, forming an *oxime*, converted by acids into an oil with an odour of carvone. The hydrocarbon is probably a homologue of dipentene having the annexed constitution, and is obtained with small amounts of an isomeride of the *terpinene* series.

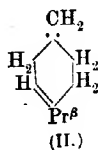
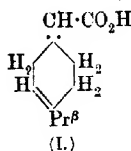
*n*-Propylnopinol,  $C_{13}H_{22}O$ , b. p. 225—235°, is formed in only small amount together with considerable quantities of nopinol by the action of magnesium *n*-propyl iodide on nopinone; it is converted by treatment with sulphuric acid into a *terpin*, which yields a crystalline *dihydrochloride*,  $C_{13}H_{20} \cdot 2HCl$ .

### III. Synthesis in the Terpinene Series.—Methylsabinaketonol

(*sabinene hydrate*), m. p. 38—39°, b. p. 195—200°, prepared by the action of magnesium methyl iodide on sabinaketone, has a terpineol odour, is stable toward permanganate, and on treatment with hydrogen bromide in glacial acetic acid solution yields *terpinene dihydrochloride*, m. p. 58—59°. When shaken with sulphuric acid, sabinene hydrate yields *terpinene dihydrochloride*, m. p. 137° (this vol., i, 238).

*Ethylsabinaketonol*,  $C_{11}H_{20}O$ , b. p. 100—104°, containing small amounts of an unsaturated substance, is prepared by the action of magnesium ethyl iodide on sabinaketone; dilute sulphuric acid converts it into a *homologue* of terpinene-terpin, which crystallises in white leaflets, m. p. 141—142°, and yields a *dihydrobromide*,  $C_{11}H_{18} \cdot 2HBr$ , m. p. 88—89°, formed also by the action of hydrogen bromide on ethylsabinaketonol in glacial acetic acid solution. The *dihydrochloride*,  $C_{11}H_{16} \cdot 2HCl$ , crystallises in plates, m. p. 67—68°; the *dihydriodide*, m. p. 88—89°; the *dihydriodide* forms prisms, m. p. 89—90°.

The action of zinc and ethyl bromoacetate on sabinaketone, with elimination of water from the resulting *hydroxy-ester*, and subsequent hydrolysis of the unsaturated *ester* leads to the formation of the unsaturated *acid* (I), m. p. 47—48°. The *silver salt*,  $C_{11}H_{15}O_2Ag$ , was analysed. On distillation, the acid loses carbon dioxide, forming a *β*-*terpene acid* (II), b. p. 176°, D 0.843,  $n_D^{20}$  0.4773, which with hydrogen chloride in glacial acetic acid solution yields *terpinene dihydrochloride*, m. p. 58—59°, and is converted by nitrous acid into *terpinene nitrosite*.



**Terpenes and Etheral Oils. LXXXIX. OTTO WALLACH**  
*Annalen*, 1907, 367, 72—84).—I. *Oxygenated Derivatives of Sylvestrene*.—The method previously described (this vol., i, 64) for substituting hydroxyl groups for halogen atoms in terpene compounds has now been applied to the formation of oxygenated derivatives of sylvestrene.

The prolonged action of hot aqueous potassium hydroxide on sylvestrene dihydrochloride leads to the formation of sylvesterpineol, which distils with steam, in a 70% yield, and sylvesterin, which remains in the alkaline distillation residue in a 25% yield.

Sylvesterin,  $C_{10}H_{18}(OH)_2$ , separates from ethyl acetate in crystals, m. p.  $155-136^\circ$ ,  $[\alpha]_D + 27.43^\circ$ .

Sylvesterpineol,  $C_{10}H_{17}OH$ , b. p.  $210-214^\circ$ , has an intense odour; with concentrated hydrochloric acid, it yields sylvestrene dihydrochloride, and is oxidised by 1% permanganate solution in the cold, yielding the alcohol,  $C_{10}H_{17}(OH)_2$ , which is obtained as a viscid, colourless oil, b. p.  $65-11$  mm. This, on oxidation with chromic and dilute sulphuric acid, yields an oil which has an aldehyde-like odour, and reduces silver solutions.

Sylvestrone,  $C_{10}H_{14}O$ , formed by removal of hydrogen chloride from sylvestrene nitrosochloride and hydrolysis of the resulting oxime by fuming oxalic acid, is obtained as an oil, and forms a semicarbazone,  $C_{10}H_{13}N:NH\cdot CO\cdot NH_2$ , crystallising in needles, m. p.  $175-177^\circ$ .

II. *Synthesis of Anethole from Anisaldehyde and of isoSafrole from Piperonal*.—[With EDGAR EVANS.]—The action of zinc and ethyl bromopropionate on anisaldehyde in benzene solution leads to the formation of the hydroxy-ester,  $OMe\cdot C_6H_4\cdot CH(OH)\cdot CHMe\cdot CO_2Et$ , b. p.  $235-245/13$  mm., which, when heated with potassium hydrogen sulphate at  $150^\circ$ , loses water and forms ethyl  $\beta$ -anisyl- $\alpha$ -methyiacrylate,  $Me\cdot C_6H_4\cdot CH:CHMe\cdot CO_2Et$ , b. p.  $170-180/25$  mm. The acid Perkin, this Journ., 1877, i, 411), when slowly distilled, loses carbon dioxide and forms anethole.

$\beta$ -Piperonyl- $\alpha$ -methyiacrylic acid,  $CH_2\begin{smallmatrix} \diagup O \diagdown \end{smallmatrix}C_6H_4\cdot CH:CHMe\cdot CO_2H$ , prepared in the same manner from piperonal and ethyl  $\alpha$ -bromopropionate, when heated loses carbon dioxide and yields isoSafrole.

III. *Occurrence of Sabinene in Ceylon Cardamom Oil and in Majorana Oil*.—A hydrocarbon, b. p.  $165-167^\circ$ , D 0.846, obtained from cardamom and Majorana oils was considered previously (this vol., i, 64) to be sabinene. As this is now confirmed by oxidation of the hydrocarbon by means of permanganate with formation of sabinic acid, it is probable that the terpene obtained from these oils by Weber (Abstr., 1887, 596) and later (Abstr., 1899, i, 535) was formed by transformation of the sabinene present (this vol., i, 229).

IV. *Iomeric Camphenes and a New Camphenecamphoric Acid*.—[With PAUL GUTMANN.]—Various observations have suggested that naturally occurring camphene melts at a lower temperature than does synthetical camphene. To determine whether this difference results from the presence of impurities in the naturally occurring hydrocarbon or from the existence of different camphenes, the authors have investigated a camphene, m. p.  $39^\circ$ , b. p.  $160-161^\circ$ , D $^{20}$  0.8555,

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$\frac{1}{2} d$

$[\alpha]_D - 84.9^\circ$ ,  $n_D^{20}$  1.46207, obtained from Siberian pinewood oil. The on oxidation with permanganate, yields a new camphenecamphoric acid,  $C_{10}H_{16}O_4$ , which crystallises in needles or leaflets, m. p.  $142^\circ$ ;  $[\alpha]_D - 1.66^\circ$ ; the silver salt,  $C_{10}H_{14}O_4Ag_2$ , was analysed. On conversion into the chloride and treatment with ammonia, the acid yields the amide,  $C_{10}H_{15}O_2N_2$ , crystallising in needles, m. p.  $197^\circ$ . The diacid,  $C_{12}H_{20}O_4N_2$ , m. p.  $218^\circ$ . The action of acetyl chloride on the acid in chloroform solution leads to the formation of a syrupy anhydride which reacts with aniline, forming an anilic acid.

Small amounts of a glycol and of an acid, which forms a sparingly soluble sodium salt, are formed together with the camphenecamphoric acid by oxidation of the naturally occurring camphene. This is converted into isoborneol by Bertram's reaction, and forms a solid hydrochloride, which, on treatment with aniline, yields a camphenecamphoric acid, m. p.  $51^\circ$ ; on bromination by Reychler's method, the camphene, m. p.  $51^\circ$ , yields a dibromide, m. p.  $89^\circ$ . In view of these facts, the naturally occurring camphene is considered to be a physical isomerite of a synthetical hydrocarbon.

A specimen of camphene obtained from citronella oil yielded on oxidation the camphenecamphoric acid, m. p.  $142^\circ$ . Another camphene, m. p.  $50^\circ$ , b. p.  $160-161^\circ$ ,  $[\alpha]_D + 103.89^\circ$ , prepared by the action of sodium nitrite on pure bornylamine in acetic acid solution, on oxidation yields a camphenecamphoric acid, m. p.  $141-142^\circ$ , which is identical with the acid obtained from the naturally occurring camphene.

**Constituents of Ethereal Oils. Teresantalic Acid,  $C_{10}H_{16}O_4$ . A New Norcamphor and its Derivatives.** FRIEDRICH SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 4465-4472). Compare this vol., i, 703.—It has been shown by Müller (*Abstr. Chem.*, i, 677) that teresantalic acid (I) is decomposed by sulphuric acid to the formation of  $\alpha$ -santene. An endeavour has now been made to study the course of this complicated reaction by employing formic in place of sulphuric acid. Here also the reaction is complicated, and leads to the formation of two products.

(a) The formate of  $\pi$ -norborneol,  $C_{10}H_{16}O_2$ , b. p.  $87-94^\circ$  mm.,  $D^{20}$  1.0092,  $n_D^{20}$  1.46559,  $[\alpha]_D - 10.15^\circ$ , when boiled with alcohol and potassium hydroxide is hydrolysed to  $\pi$ -norborneol (II), m. p.  $68-70^\circ$ , b. p.  $87-88^\circ$ , which is optically inactive. The acetate,  $C_{12}H_{20}O_4$ , b. p.  $89-90.5^\circ/9$  mm.,  $D^{20}$  0.987,  $n_D^{20}$  1.45962.

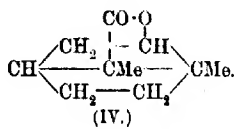
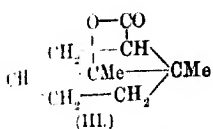
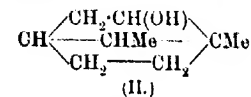
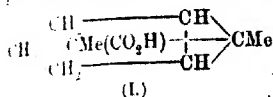
$\pi$ -Norcamphor,  $C_{10}H_{14}O$ , formed by oxidation of  $\pi$ -norborneol with chromic acid in glacial acetic acid solution, has m. p. about  $50^\circ$ , b. p.  $75-76^\circ/9$  mm.,  $D^{20}$  0.966,  $n_D^{20}$  1.46900, is optically inactive, and on treatment with sodium and isoamyl formate in ethereal solution yields an  $\alpha$ -methylene derivative,  $C_{10}H_{14}O_2$ , b. p.  $110-113^\circ/9$  mm.,  $D^{20}$  0.941,  $n_D^{20}$  1.50045, which gives an intense bluish-violet coloration with ferric chloride.

$\pi$ -Norisoborneol,  $C_{10}H_{16}O$ , m. p.  $91-92^\circ$ , b. p.  $88^\circ/9$  mm., is prepared by reduction of the ketone with sodium and alcohol.

(b) The lactone (III), m. p.  $190^\circ$ , on reduction with sodium and alcohol forms a glycol, m. p.  $254^\circ$ , which when distilled with steam

teresa of sulphuric acid yields a volatile oxide,  $C_{10}H_{16}O$ , m. p.  $148^{\circ}$ . The hydroxy-acid,  $C_{10}H_{16}O_3$ , m. p.  $196^{\circ}$ , corresponding to the lactone, forms an ethyl ester,  $C_{11}H_{18}O_3$ , b. p.  $125^{\circ}/9$  mm.,  $D^{20}_D$  1.098,  $n^{20}_D$  1.4816.

The lactone (IV), m. p.  $103^{\circ}$ , obtained by Müller (*loc. cit.*) from teresantallic acid hydrochloride, is reduced to a glycol,  $C_{10}H_{18}O_2$ , b. p.  $165-166^{\circ}/10$  mm. Hydrolysis of the lactone leads to the formation of a hydroxy-acid,  $C_{10}H_{16}O_3$ , m. p.  $159^{\circ}$ , which forms an ethyl ester, b. p.  $120-123^{\circ}/9$  mm.,  $D^{20}_D$  1.089,  $n^{20}_D$  1.48228.



It remains undecided whether the two lactones and their hydroxy-acids are structurally or stereo-chemically isomeric. The constitutional formulæ given are ascribed to teresantallic acid and its derivatives on the former supposition, which necessitates the assumption that various hypothetical intermediate products are formed by the action of formic acid on teresantallic acid.

G. Y.

**The Present Position of the Chemistry of Rubber.** SAMUEL PERLES (*Brit. Assoc. Reports*, 1906, 76, 233-257).—A résumé of the different methods employed in attacking the problem of the chemical constitution of rubber.

G. T. M.

**The Cyanogenetic Glucoside of Flax. (Linseed.)** WYNDHAM DUNSTAN and THOMAS A. HENRY (*Bull. Acad. roy. Belg.*, 1907, 790-791).—LINAMARIN. ARMAND JORISSEN (*ibid.*, 793-798).—Polemical reference to the question whether the name phaseolunatin or linamarin should be used for this glucoside (see Jorissen and Hairs, *Ann.* 1885, 181; 1892, 502; Jouck, *Diss. Strasbourg*, 1902; Dunstan and Henry, *Abstr.*, 1904 ii, 711; Jorissen, this vol., i, 434).

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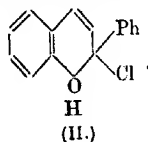
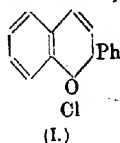
**Bromo-derivatives of Dimethyl- and Trimethyl-furandicarboxylic Acids.** HYPOLYT TREPHILIEFF (*Ber.*, 1907, 40, 4388-4390).—Complicated changes occur when these acids are brominated in aqueous solution. Tetrabromo-derivatives are, however, obtained from methronic acid, ethyl methronate, and methyl methronate by using these substances to the action of bromine vapour at the ordinary temperature for two to three weeks. Nitric acid oxidises tetrabromomethronic acid to oxalic acid; lead peroxide oxidises this acid to malic acid.

Condensation of maleic acid and ethyl acetoacetate in the presence



of acetic anhydride results in the formation of a compound,  $\text{C}_{10}\text{H}_7\text{O}_2\text{Cl}$ , of m. p.  $137^\circ$ .

**Benzopyryronium and Higher Homologous and Isologous Pyryronium Rings.** HERMAN DECKER and THEODOR VON FELLESEN (*Annalen*, 1907, 366, 281—342. Compare this vol., i, 1569). The oxygen-free salts of triphenylcarbinol having been recognised as carbonium salts, the constitution of the substances described as salts of xanthonium (Bünzly and Decker, *Abstr.*, 1904, i, 1612) and coeroxonium (Decker, *Abstr.*, 1906, i, 687) and their sulphur isologues, and of dinaphthoxonium and coerdioxonium (Decker, *ibid.*, 1906, i, 687), became doubtful, since these possess the atomic groupings of di- and tri-phenylcarbinol and may equally be carbonium salts. In favour of the oxonium constitution is the difference in the basicities of tri-phenylcarbinol and phenylxanthanol; whilst salts of the former are not formed by the action of hydrochloric acid and are decomposed by 70% sulphuric acid, phenylxanthonium salts are stable in 10% sulphuric acid and are readily formed by means of hydrochloric acid. Moreover, the sulphur isologues are more strongly basic than the oxygen compounds in agreement with the known greater stability of the former than oxonium salts. It is now found that the action of magnesium phenyl bromide on coumarin or of concentrated hydrochloric acid on *o*-hydroxybenzylideneacetophenone leads to the formation of a substance which must be 2-phenylpyryronium chloride (I), as a substance having the other possible constitution (II) would not be a salt.



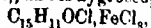
It is argued that as the benzopyryronium salts are isologues of the quinolonium series, so the salts of xanthonium and thioxanthonium must be isologous with the acridonium and those of coeroxonium with the coeramidonium (Decker, Ferrario, and Sella, *Abstr.*, 1906, i, 690) derivatives. The preparation and properties of a number of salts of benzopyryronium, xanthonium, coeroxonium, and their isologues are described.

*Benzopyryronium chloride*, prepared by heating gluco-*o* coumarilic acid with concentrated hydrochloric acid, is readily soluble; the *ferric chloride*,  $\text{C}_{10}\text{H}_7\text{OCl}_2\text{FeCl}_3$ , forms a yellow, crystalline powder, m. p.  $199^\circ$  (corr.), and when heated with aqueous acetone gives an oil of fennel; the *aurichloride*,  $\text{C}_{10}\text{H}_7\text{OCl}_2\text{AuCl}_3$ , crystallises in brownish-yellow, microscopic needles, m. p.  $198\text{--}200^\circ$  (corr.).

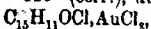
*2-Methylbenzopyryronium ferrichloride*,  $\text{C}_{10}\text{H}_7\text{OCl}_2\text{FeCl}_3$ , prepared from *o*-hydroxycinnamyl methyl ketone, crystallises in yellow needles, m. p.  $118\text{--}119^\circ$  (corr.). The *cadmiobromide*,  $\text{C}_{10}\text{H}_7\text{OBr}_2\text{CdBr}_2$ , forms a yellow, crystalline powder. The free base is unstable and readily changes into a dye. The *iodide*,  $\text{C}_{10}\text{H}_7\text{OI}$ , prepared from coumarilic acid and magnesium methyl iodide, crystallises in greenish-brown needles.

m. p. 140–60°, readily loses iodine, and when heated with aqueous hydrochloric acid is decomposed, forming coumarin.

*3-Benzopyryronium chloride*,  $C_{15}H_{11}OCl$ , crystallises in yellow needles, m. p. 69–70° (corr.), and is hygroscopic. The *ferrichloride*,



yellow needles, m. p. 125–129° (corr.), *aurichloride*,



m. p. 200–202°, *mercurichloride*, brownish-yellow needles, m. p.

183–185°, *cadmibromide*,  $C_{15}H_{11}OBr, CdBr_2$ , brownish-yellow needles,

m. p. 190–192°, *perbromide*,  $C_{15}H_{11}OBr, Br_2$ , orange-red crystals, m. p.

127°, *periodide*,  $C_{15}H_{11}OI, I_2$ , m. p. 147–148°, unstable, and *iodide*,

orange-red crystals, are described. A *by-product* from the action of

magnesium phenyl bromide on coumarin, which is

Ph insoluble in hydrochloric acid, will be described later

(compare Houben, Abstr., 1904, i, 302, 334). The

OH action of sodium hydroxide and much water on the

chloride leads to the formation of a greenish-brown

precipitate containing the *carbinol base*, which has the annexed con-

stitution, and is obtained also by the action of ammonia on the chloride

in aqueous solution.

[With FAIRZ DINNER.]—9-*o*-Tolylxanthen-9-ol,



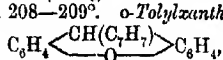
prepared from xanthone and magnesium *o*-tolyl bromide (compare

loc. cit.), crystallises from benzene in colourless

needles, and loses  $\frac{1}{2} C_6H_5$  at 110°; m. p. 150.5°. *o*-Tolylxanthonium

*chloride*,  $C_6H_4 \left\langle \begin{array}{c} C(C_7H_7) \\ OCl(FeCl_3) \end{array} \right\rangle C_6H_4$ , crystallises in yellowish-

green needles, m. p. 208–209°. *o*-Tolylxanthen,



prepared by boiling *o*-tolylxanthenol with hydriodic acid and red

phosphorus in acetic anhydride solution, crystallises in colourless

plates, m. p. 119°, and dissolves in cold sulphuric acid, forming the

xanthonium salt. A *substance*,  $C_{23}H_{19}O_3$  or  $C_{23}H_{20}O_3$ , crystallises in

plates, m. p. 162°, a *hydrocarbon*,  $(C_{14}H_{13})_x - (C_9H_8)_z$ , m. p. 214°, a

*substance*, crystallising in leaflets, m. p. 170°, are obtained as

products of the action of magnesium *o*-tolyl bromide on

xanthone.

*3-Methoxy-3-phenylxanthonium ferrichloride*,  $C_{20}H_{15}O_3Cl, FeCl_3$ ,

OH Ph prepared from 3-methoxyxanthone and mag-

nesium phenyl bromide, forms dark red crystals,

m. p. 124°, and on treatment with water yields

3-methoxy-3-phenylxanthen-9-ol, m. p. 133°.

This has the annexed constitution, and with

acids yields *oxonium* salts which are stable in

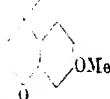
10% hydrochloric acid and form deep red,

fluorescent solutions.

*3-Methoxy-3-phenylxanthonium ferrichloride*, prepared from

3-methoxyxanthone, crystallises in needles, m. p. 151°, and is more

soluble to water and more deeply coloured than its isomeride.

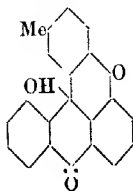


[With ENOS FERRARIO].—The green, fluorescent solution obtained on dissolving fluoran in concentrated sulphuric acid contains 9-o-carboxyphenylxanthonium sulphate, which is stable only in concentrated acid. The ferrichloride,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}_{13}\text{H}_9\text{O}_4\text{Fe}$ , prepared by adding hydrochloric acid containing solid ferric chloride to a hot solution of fluoran in acetic acid, crystallises in yellow needles, m. p. 200°. Fluoran does not form a xanthonium salt on fuming hydrochloric acid; this difference in behaviour from the other members of the group results, not only from the negative induction of the carboxylic group, but also from the tendency of the carbinol base to lactone formation.

Dimethylfluoran forms a xanthonium ferrichloride,  $\text{C}_{22}\text{H}_{17}\text{O}_4\text{Fe}$ , crystallising in orange needles, m. p. 215°.

Coeroxonol (Abstr., 1906, i, 688) forms ethers when boiled with corresponding alcohols. The methyl ether,  $\text{C}_{21}\text{H}_{14}\text{O}_3$ , crystallises in yellow needles, m. p. 133°. The n-propyl ether,  $\text{C}_{23}\text{H}_{18}\text{O}_3$ , m. p. 151°. The isobutyl ether,  $\text{C}_{24}\text{H}_{20}\text{O}_3$ , m. p. 132°. These ethers are convertible into each other; thus the methyl ether is formed when the ethyl ether is boiled with a large excess of methyl alcohol. Coeroxonol condenses readily with acetone, forming acetonylcoeroxone, m. p. 146°, and yields coeroxonium salts when heated with hydrochloric or sulphuric acid.

[With LEO STERN].—Erythroxyanthraquinone p-tolyl ether,  $\text{C}_{21}\text{H}_{14}\text{O}_3$ , prepared as described in D.R.-P. 158531 (Abstr., 1906, i, 77), crystallises in yellow needles, m. p. 128.5°, and, when heated with fuming sulphuric acid and treated with ferric chloride, yields 14-methylcoeroxonium ferrichloride,  $\text{C}_{21}\text{H}_{13}\text{O}_2\text{Cl}\cdot\text{FeCl}_3$ , which is obtained in reddish-brown crystals, m. p. 232.5–235.5°, has the properties characteristic of coeroxonium salts, and becomes colourless on treatment with water. 14-Methylcoeroxone-9-ol (corrected formula) separates from benzene in colourless crystals, m. p. 176°, and reacts with acids, forming the dimethylcoeroxonium salts. The ethyl ether,  $\text{C}_{23}\text{H}_{16}\text{O}_3$ , crystallises in needles, m. p. 139°.

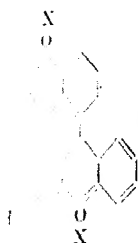


[With ENOS FERRARIO].—4:14-Dimethylcoeroxone-9-ol, previously described (Abstr., 1906, i, 688) and 3:13-dimethylcoeroxonol, has m. p. 170° (152° *loc. cit.*). The methyl ether,  $\text{C}_{22}\text{H}_{15}\text{O}_3$ , forms colourless crystals, m. p. 105°. The ethyl ether,  $\text{C}_{24}\text{H}_{17}\text{O}_3$ , m. p. 145°. The action of mineral acids on the carbinol leads to the formation of coeroxonium salts; the ferrichloride, m. p. 210° (160° *loc. cit.*). The reduction of the carbinol base or of the oxonium salts leads to the formation of 4:14-dimethylcoeroxen-10-ol, which has a strong green fluorescence, dissolves in aqueous sodium hydroxide, forming an orange-red solution, and is very readily oxidised. The acetate is obtained in yellow crystals, m. p. 230°.

[With AUGUST WÜRSCH].—1-Thiolanthraquinone p-tolyl ether,  $\text{C}_{21}\text{H}_{14}\text{O}_2\text{S}$ , prepared from potassium α-anthraquinonesulphonate, p-thiocresol, and potassium hydroxide, or from nitroanthraquinone, crystallises in orange-red needles, 223–225°, and when heated with fuming sulphuric acid yields the 14-methylcoerthionium salt, which

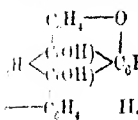
obtained as the *ferrichloride*,  $C_{21}H_{11}OSCl_2FeCl_3$ , obtained in blackish-green crystals, m. p. 240°. 14-*Methylcoerthione-9-ol*,  $C_{21}H_{14}O_4S$ , formed by the action of water on the thionium salt, separates from benzene as a white, crystalline powder, m. p. 235°, and on reduction yields 14-*methyldithione-10-ol*,  $C_{21}H_{14}OS$ , m. p. 247°, which forms yellow crystals with green fluorescence, and is soluble in alkalis.

With Exos FERRARIO.]—When heated with phosphoric acid or a



mixture of phosphoric and sulphuric acids, anthra-rufin diphenyl ether is converted into coerdioxonium salts having the constitution (I). The *ferrichloride*,  $C_{26}H_{14}O_3Cl_3 \cdot 2FeCl_3$ , is obtained as a black, crystalline precipitate. The *sulphate*, *hexabromide*, and *iodide* are described. When treated with water, the ferrichloride yields *coerdithiendiol* (II), which separates as a violet, crystalline powder, forms violet-blue to violet-red solutions with intense, brownish-red fluorescence, and is reduced to *coerdioxen*. This forms an orange-red precipitate, sublimes, forming a

sublimate, dissolves in ether or benzene to an orange solution with intense green fluorescence, and is readily oxidised, yielding the dioxonium salts.



1:5-Dithiolanthraquinone diphenyl ether,  $C_{26}H_{18}O_2S_2$ , prepared by boiling dinitroanthraquinone, thiophenol, and potassium hydroxide in alcoholic solution, crystallises in orange-red

crystals, m. p. 247°, and on prolonged heating at 200° and treatment with sulphuric acid and ferric chloride yields *coerdithionium ferrichloride*,  $C_{26}H_{14}S_2Cl_3 \cdot 2FeCl_3$ , which forms black crystals, with a green tinge when powdered, m. p. 258–260°; the *hexabromide* forms an orange-green precipitate. *Coerdithiendiol*, formed by the addition of water to the coerdithionium salts, separates from glacial acetic acid in colourless crystals, m. p. 248°, yields a coloured, fluorescent solution if strongly heated in acetic acid, and is reduced to *coerdithien*, which is obtained as an orange precipitate, sublimes unchanged, forms fluorescent solutions, and is readily oxidised to the dithionium salts.

1:5-Dithiolanthraquinone di-p-tolyl ether,  $C_{28}H_{20}O_2S_2$ , prepared from p-cresol, potassium hydroxide, and dinitroanthraquinone, forms reddish-brown crystals, m. p. 249°. *Dimethylcoerdithionium ferrichloride* forms black crystals, m. p. 204°. *Dimethylcoerdithienol* is colourless. *Dimethylcoerdithien* is yellowish-red, forms solutions with green fluorescence, and is readily oxidised to the dithionium salts.

The isologous coerdiamidonium compounds have been previously described (Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1902, i, 121).

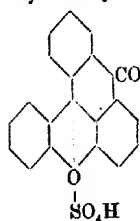
The relation of the coeroxonium salts to the coeroxonols and the similar relations in the isologous series are discussed in the light of Erlenmeyer's theory of partial valencies.

G. Y.

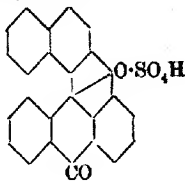
**Preparation of Coeroxonium and Coerthionium Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 186882. *Chem. Abstr.*, 1905, i, 797; 1906, i, 687).—The aryl ethers and aryl

thioethers of the anthraquinone series when condensed with certain acid dehydrating agents give rise to coeroxonium and coerthionium derivatives, which are used in the preparation of colouring matter.

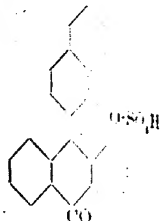
*Coeroxonium sulphate* (I) results from the dehydrating action of 70% sulphuric acid or zinc chloride on 1-phenoxyanthraquinone (1-phenoxyanthraquinone phenyl ether):



(I.)



(II.)

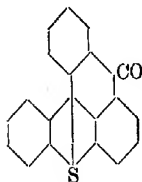


(III.)

The free coeroxonium base (coeroxonol; *loc. cit.*), a white crystalline precipitate, is set free from the sulphate by ammonia; its ethyl ether,  $C_{22}H_{16}O_3$ , m. p.  $145^\circ$ , is a well-defined, crystalline substance.

*Coeroxonium ferrichloride*,  $C_{20}H_{11}O_3Cl_2FeCl_3$ , m. p.  $233^\circ$ , is obtained in dark red crystals on adding ferric chloride and strong hydrochloric acid to the sulphate solution.

Benzocoeroxonium salts are obtained when the  $\beta$ -naphthyl ether of 1-hydroxyanthraquinone are employed in the foregoing condensation.



(IV.)

*Benzocoeroxonium sulphate* (II), the corresponding chloride, and the ferrichloride,  $C_{24}H_{13}O_3Cl_2FeCl_3$ , are sparingly soluble, dark violet, crystalline salts. The free base, *benzocoeroxonol*, m. p.  $186-187^\circ$ , separates in almost colourless crystals.

*isoBenzocoeroxonium sulphate* (III) is obtained in a similar manner from  $\alpha$ -naphthyl-1-oxyanthraquinone.

*Coerthionium sulphate* (IV) is a violet red salt resulting from the condensation of phenyl-1-thioanthraquinone; its carbinol base may be crystallised from alcohol. Coerthionium salts are generally more intensely coloured than the corresponding coeroxonium derivatives.

G. T. M.

**Action of Grignard's Reagent on Cinchoninicine.** Enzo Cocucci (*Boll. chim. Farm.*, 1907, 46, 753-756).—With magnesium ethyl iodide, cinchoninicine yields a pale yellow, amorphous, addition compound, which is stable when kept in a sealed tube or over sulphuric acid. This compound no longer contains the ketonic or vinyl group, and, when treated with dilute sulphuric acid, it yields a product which, after repeatedly dissolving in hydrochloric acid and precipitating with ammonia, has the composition  $NH_2C_{16}H_{18}N(CEt.OH).CH_2.CH_2.Et$  or  $NH_2C_{16}H_{18}N(CEt.OH).CHMeEt$ .

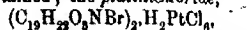
T. H. P.

**Action of Halogen on Morphine Derivatives.** Eugène Vongebichten and O. Densdorff (*Ber.*, 1907, 40, 4146-4154).—A

Continuation of the work of Vongerichten and Hübner (this vol., i, 235), who studied the action of bromine on morphine, codeine,  $\alpha$ - and  $\beta$ -acetylmorphimethine and dihydromethylmorphimethine respectively.

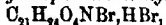
Acetyl- $\alpha$ -methylmorphimethine, in dilute acetic acid solution, behaves like  $\alpha$ -methylmorphimethine in uniting with only 1 mol. of bromine; in more concentrated acetic acid solution, 3 atoms of bromine are added on.

*Acetyldibromodihydro- $\alpha$ -methylmorphimethine hydrobromide*,  $(C_{19}H_{23}O_4NBr_2) \cdot HBr$ , has m. p. about  $202^\circ$  (decomp.); the *platinichloride*,  $(C_{19}H_{23}O_4NBr_2) \cdot H_2PtCl_6$ , was prepared. By the action of sodium cyanide on acetylbromo- $\alpha$ -methylmorphimethine, bromo- $\alpha$ -methylmorphimethine was obtained; the *platinichloride*,



and the *methiodide*  $C_{19}H_{23}O_4NBr \cdot MeI$ , were prepared.

*Acetylbromo- $\alpha$ -methylmorphimethine hydrobromide*,



obtained by boiling acetyldibromodihydro- $\alpha$ -methylmorphimethine hydrobromide with acetic anhydride, separates from water in glistening needles, decomposing at  $235^\circ$ .

*Acetylnor-p-thebaine methobromide*,  $C_{21}H_{25}O_4NBr$ , obtained by heating acetyldibromodihydro- $\alpha$ -methylmorphimethine with acetic anhydride, crystallises in needles or prisms, m. p.  $231-233^\circ$ . *Acetylnor-p-thebaine methiodide*, formed by the addition of potassium iodide to the preceding compound, has m. p.  $236^\circ$ . *Nor-p-thebaine methiodide*,  $C_{19}H_{23}O_4NI$ , has m. p.  $220^\circ$ .

A. McK.

**Preparation of Sulphonic Acids of Acetyl Derivatives of Morphine.** KNOTT & Co. (D.R.-P. 195601. Compare this vol., i, 235).

When morphine is gently heated with a mixture of acetic anhydride and sulphuric acid which no longer gives the reactions of sulphuric acid, it is converted into triacetylmorphine. When, however, the reaction is carried out at temperatures lower than that required to convert acetyl sulphuric acid into sulphoacetic acid, then the base is simultaneously acetylated and sulphonated. The product, *diacetyl-morphine-sulphonic acid*, is precipitated by ether from its aqueous or alcoholic solutions as a white powder, which on acidifying separates from its alkaline solution in clusters of needles not melting below  $280^\circ$ . As generally the case, the introduction of the sulphonic group greatly diminishes the toxic action of morphine.

G. T. M.

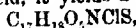
**Intermediate Product in the Formation of apoMorphine.**

LEONZ ACH and HERMANN STEINBOCK (*Ber.*, 1907, 40, 4281-4285).

The restricted action of hydrochloric acid on morphine yields a compound, termed by the authors  $\beta$ -chloromorphide, which is isomeric with Schryver and Lees' chloromorphide (*Trans.*, 1900, 77, 1024), and can also be prepared from the latter by the gentle action of hydrochloric acid.

*$\beta$ -Chloromorphide*,  $C_{17}H_{19}O_2NCl$ , crystallises from ether in a drusy mass of prisms or from alcohol in prisms, m. p.  $188^\circ$ , and is more readily soluble in alcohol or benzene than its isomeride. When freshly precipitated from its salts,  $\beta$ -chloromorphide is readily soluble in ether, but after one crystallisation it dissolves only sparingly in this solvent.

Its salts are mostly readily soluble, but the *nitrate* separates in glassy prisms. With sulphuric acid, it yields a *sulpho-derivative*.



which crystallises from water in glassy prisms containing  $11H_2O$ ; it has a neutral reaction in aqueous solution; the *sulpho-compound* yields a crystalline *acetyl* derivative, and, when heated with water at  $140^\circ$ , it is converted into a crystalline *sulpho-compound* free from chlorine.

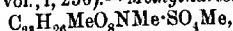
The isomeric chloromorphide (*loc. cit.*) yields no crystalline *sulpho-derivative*.

*$\beta$ -Chloromorphide methiodide*,  $C_{18}H_{21}O_2NCH_2I$ , separates from water in dense crystals, m. p.  $210^\circ$  (decomp.), and is decomposed when heated with an aqueous alkali, yielding a volatile base.

*Acetyl- $\beta$ -chloromorphide*,  $C_{19}H_{20}O_2NCl$ , crystallises from alcohol in needles, m. p.  $163^\circ$ , and yields a *methiodide*, m. p.  $177^\circ$  (decomp.).

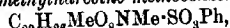
T. H. P.

**Preparation of Additive Products of Alkylnarceine or Alkyl homonarceine and their Alkyl Ethers.** KNOLL & Co. (D.R.P. 186884. Compare this vol., i, 236).—*Methylnarceine methosulphate*,

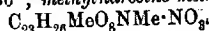


m. p.  $184-186^\circ$ , formed by the interaction of narceine (1 mol.) and methyl sulphate (2 mols.) in alcoholic potassium hydroxide; its hydrochloride decomposes at  $196^\circ$ . The following compounds are also described.

*Ethylnarceine ethiodide*,  $C_{23}H_{26}EtO_8NEtI$ , m. p.  $140-144^\circ$ , produced by the combination of ethylnarceine and ethyl iodide at  $80^\circ$ ; *homonarceine methiodide*,  $C_{23}H_{25}EtO_8NMeI$ , m. p.  $184-185^\circ$ ; *dimethylnarceine methophosphate*,  $C_{23}H_{26}MeO_8NMe \cdot PO_3Me_2$ , its hydrochloride, m. p.  $136^\circ$ ; *methylnarceine methobenzene-sulphonate*,

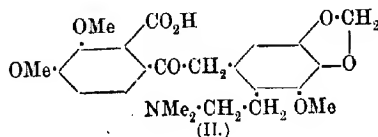
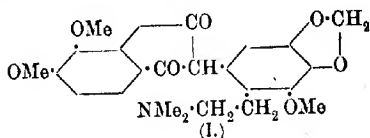


hydrochloride, m. p.  $136^\circ$ ; *methylnarceine methonitrate*,

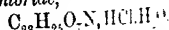


G. T. M.

**Preparation of apoNarceine.** KNOLL & Co. (D.R.P. 187133. Compare this vol., i, 236).—*apoNarceine* (I), yellow needles, m. p.  $112-115^\circ$ , is obtained by treating narceine (II) with dehydrating



agents, such as mineral acids, acid chlorides, or acid anhydrides; it is extracted with ether and converted into its *hydrochloride*,



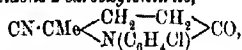
yellow needles, m. p.  $144^\circ$ . This salt is only sparingly soluble in cold water, but dissolves more readily on warming; it gives the ordinary alkaloid reactions. *apoNarceine*

is insoluble in water, but dissolves readily in the organic

from media, excepting light petroleum; when warmed with alkalis, it is reconverted into narceine. The *aponarceine methosulphate* is soluble from alcohol and ether in needles; it forms similar compounds with other alkyl halides, sulphates, and phosphates.  
G. T. M.

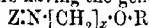
**Anisothobromine.** VON SZTANKAY (*Chem. Zentr.*, 1907, i, 1806; *Pharm. Post*, 1907, 40, 322).—*Anisothobromine* (sodium *theobromine anisate*),  $\text{NaC}_7\text{H}_7\text{O}_2\text{N}_4\cdot\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ , is a white, slightly hygroscopic powder, melting and decomposing when carefully heated. It precipitates theobromine and anisic acid from its aqueous solution.  
W. H. G.

**Condensation Products of Ethyl Lævulate, Hydrogen Cyanide, and Para-substituted Anilines.** HERMANN WEBER (*Ber.*, 1907, 40, 3044—4052. Compare Kühling and Falk, *Abstr.*, 1905, i, 111).—The author's aim is to ascertain the influence of negative substituents on the stability of the pyrrolidone nucleus. The condensations were carried out in alcoholic solution on the water-bath. 1-*p*-Chloro-2-methylpyrrolidone-2-carboxylonitrile,



the *amide*, and the *carboxylic acid* have m. p. 40—42°, 207°, and 179° respectively. The corresponding *compounds*, obtained from *p*-bromocyanide, have m. p. 49—51°, 208°, and 189° respectively; the *barium chloride* salts and the *methyl ester* were prepared. The nitrile yields *ureamide* with ammonium sulphide, and  $\gamma$ -oximinovaleic acid by treatment with hydroxylamine hydrochloride. 1-*p*-Iodophenyl-2-methylpyrrolidone-2-carboxylonitrile is an oil, from which the *amide*, m. p. 222°, and the *carboxylic acid*, m. p. 211—212°, are readily obtained. *p*-Aminobenzonitrile condenses with hydrogen cyanide and ethyl lactate to form an oil from which well-defined derivatives have been obtained. Ethyl *p*-aminobenzoate condenses readily to form *ureol*-bases,  $\text{CN}\cdot\text{CMe}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , m. p. 75°, from which the *dicarboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{CMe}\left\langle\begin{array}{c}\text{CH}_2-\text{CH}_2 \\ \text{N}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})\end{array}\right\rangle\text{CO}$ , m. p. 228—229°, is obtained by hydrolysis; the *ethyl ester-amide*,  $\text{NH}\cdot\text{CO}\cdot\text{CMe}\left\langle\begin{array}{c}\text{CH}_2-\text{CH}_2 \\ \text{N}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et})\end{array}\right\rangle\text{CO}$ , has m. p. 149°, and the corresponding *methyl ester-amide*, 171—172°. C. S.

**Preparation of Amino-Ethers.]** EMANUEL MERCK (D.R.-P. 1906).—The amino-ethers having the general formula



are obtained by treating the halogenated ethers,  $\text{X}\cdot[\text{CH}_2]_x\cdot\text{O}\cdot\text{R}$ , with secondary amines. The hydrochlorides of these amino-ethers give neutral solutions and have a powerful anaesthetic action.

*Guaiacyl  $\epsilon$ -dimethylaminoamyl ether*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_5\cdot\text{NMe}_2$ , m. p. 144—145°, was produced by mixing guaiacyl  $\epsilon$ -bromoamyl ether with dimethylamine in closed vessels; its hydrochloride is soluble. *Isopropylpropyl phenyl ether*,  $\text{Ph}\cdot\text{O}\cdot[\text{CH}_2]_3\cdot\text{C}_6\text{H}_{10}$ , b. p. 150°/10 mm.,



*ε*-Piperidylamyl phenyl ether,  $\text{Ph} \cdot \text{O} \cdot [\text{CH}_2]_5 \cdot \text{NC}_5\text{H}_{10}$ , b. p. 173°/3 mm.  
*γ*-Piperidylpropyl guaiacyl ether,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot [\text{CH}_2]_3 \cdot \text{NC}_5\text{H}_{10}$ , b. p. 173°/10 mm.  
*ε*-Piperidylamyl guaiacyl ether,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot [\text{CH}_2]_5 \cdot \text{NC}_5\text{H}_{10}$ , b. p. 190°/5 mm.  
*ε*-Piperidylamyl menthyl ether,  $\text{C}_{10}\text{H}_{18} \cdot \text{O} \cdot [\text{CH}_2]_5 \cdot \text{NC}_5\text{H}_{10}$ , b. p. 170—172°/4 mm.  
*ε*-Piperidylpropyl thymyl ether, b. p. 177—178°/6 mm.  
*ε*-Piperidylamyl thymyl ether, b. p. 200—202°/5 mm.  
*ε*-Camphidylamyl thymyl ether,  $\text{C}_{10}\text{H}_{18} \cdot \text{O} \cdot [\text{CH}_2]_5 \cdot \text{NC}_5\text{H}_{10}$ , b. p. 122—123°, were all prepared in a similar manner to the corresponding brominated mixed ethers. G. T. M.

**Preparation of Pyrimidine Derivatives.** EMANUEL MERO (D.R.-P. 185963).—Pyrimidine derivatives having the general formula  $\text{R}^{\text{I}} \cdot \text{C} < \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{R}^{\text{III}} \\ \text{NH} \cdot \text{C} \cdot \text{R}^{\text{V}} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{R}^{\text{II}} \\ \text{R}^{\text{IV}} \end{smallmatrix}$ , are obtained by condensing carbonyl thiocarbamide, guanidine, or their derivatives with alkyl malonates, malonamates, or cyanoacetates, or with malononitrile, or mono- and di-alkyl derivatives of substituted malonic acids in the presence of chlorides of the alkali or alkaline earth metals.

4-Iminobarbituric acid results from the condensation of carbonyl ethyl cyanoacetate, and sodium carbide in xylene solution, being precipitated from the resulting alkaline solutions with acetic acid. 5:5-Diethylbarbituric acid is similarly obtained from carbamide ethyl diethylmalonate, and sodium carbide. G. T. M.

**Hydroxypyridinechromium Salts. Additive Salt Formation with Metallic Hydroxides.** PAUL PEIFFER (and W. OBER, *Ber.*, 1907, 40, 4026—4036).—The monohydroxylo-, dihydroxylo-, and trihydroxylo-compounds, derived from chromiumtetra-aquopyridine, were found to form salts with acids by direct addition (Abstr., 1906, i, 531). Such additive salt-formation has been stated also in the case of other metallic hydroxides (this vol., i, 895, 1904; Werner, this vol., i, 189, 239; ii, 560). The present paper contains an account of further observations made with members of the pyridine chromium series.

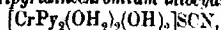
The hydroxylo-salts, derived from chromiumtetra-aquopyridine, are prepared by three methods: (1) the removal of a mol. of acid from an aquo-salt by the action of a base; (2) the gradual addition of acid to a polyhydroxylo-compound, which leads finally to the formation of the tetra-aquo-salt, and (3) the action of normal salts on tetra-aquo-salts in aqueous solution, which leads only in certain cases to the formation of hydroxylo-salts in consequence of partial hydrolysis of the tetra-aquo-salt in solution.

Hydroxylotriaquodipyridinechromium thiocyanate and sulphate have now been prepared by the action of ammonium thiocyanate and sulphate respectively on dihydroxylodiaquodipyridinechromium chloride in acetic acid solution.

*Dihydroxylodiaquodipyridinechromium iodide*,  $[\text{CrPy}_2(\text{OH})_2(\text{OH}_2)_2]\text{I}$ , is formed by addition of potassium iodide to the dihydroxylo-chloride in acetic acid solution or to the monohydroxylothiocyanate in aqueous

is called as a greenish-grey powder, and on treatment with a mineral acid yields the corresponding tetra-aquo-salt.

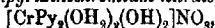
*Tetrahydroxydipyrindinechromium thiocyanate*,



prepared by adding pyridine to the monohydroxylo-thiocyanate in absence of water, or by addition of ammonium thiocyanate to an aqueous solution of a soluble dihydroxylo-salt, forms a greyish-brown powder, has a slight alkaline reaction in aqueous solution, and forms a red tetra-aquo-salt on treatment with mineral acids.

*Dihydroxydipyrindinechromium sulphate* forms a greyish-green aqueous solution, which appears reddish-brown in thick layers, becomes red on addition of mineral acids, and yields the chloride and nitrate as greyish-green precipitates on addition of sodium chloride and sodium nitrate respectively.

*Dihydroxydipyrindinechromium nitrate*,



is obtained when chromiumtrihydroxyloaquodipyrindine is treated with small amount of nitric acid, or by the action of pyridine on tetra-aquodipyrindinechromium nitrate in aqueous solution; it is obtained as a greyish-grey powder, has a very slight alkaline reaction, does not form an oxide with aqueous silver nitrate, gives precipitates of the corresponding dihydroxylo-salts when treated with sodium chloride, sodium bromide and iodide, and ammonium thiocyanate, and is converted into red tetra-aquo-salts by the action of mineral acids.

*Tetraaquodipyrindinechromium nitrate*,  $[\text{CrPy}_2(\text{OH})_2](\text{NO}_3)_2$ , prepared by addition of concentrated nitric acid to the preceding salt and evaporation over soda-lime, forms light red leaflets, is deliquescent, dissolves, forming red solutions in water and alcohol, and gradually decomposes to a dirty green, viscid mass. G. Y.

[Preparation of Isatin Derivatives.] KALLE & Co. (D.R.P. 2250 and 182261).—The condensation of isatin and 3-oxy-1-thio-aphthalen in hot aqueous sodium carbonate leads to the production of a very sparingly soluble colouring matter, having probably the constitution:  $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C} : \text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NH}.$

This substance furnishes a soluble reduction product on treatment with alkaline reducing agents. When isatinacetic acid is substituted for isatin in this condensation, a colouring matter is produced which gives a soluble sodium salt separating in lustrous, bright red crystals. This substance is a wool dye of considerable fastness.

G. T. M.

**Asymmetric Nitrogen. XXX. Resolution of a Cyclic Asymmetric Ammonium Base.** EDGAR WEDEKIND and O. VIEKING (*Ber.*, 1907, 40, 4450—4456. Compare Buckney, this vol. i. 722).—The authors have resolved methylallyltetrahydro-*endo*-d-bromocamphorsulphonate by recrystallisation from a mixture of solvents. The less soluble *l*-base-*d*-acid salt has  $[\alpha]_D + 39.09^\circ$ ,  $M_D + 194.7^\circ$ , and on treatment with concentrated aqueous potassium hydroxide yields the *iodide*,  $[\alpha]_D + 20.57^\circ$ ,  $[M]_D - 64.98^\circ$ , which rapidly

undergoes racemisation when dissolved in methyl alcohol. The more soluble *d*-base *d*-acid salt has  $[\alpha]_D +76.48^\circ$ ,  $[M]_D +380.7$ . These values give  $[M]_D -80.3^\circ$  and  $+105.7^\circ$  for the *l*- and *d*-acids respectively. On further fractional recrystallisation, a fraction having  $[M]_D +434^\circ$  was obtained; this yields an iodide which after recrystallisation is optically inactive.

*Benzylmethyltetrahydroquinolinium bromide* undergoes partial decomposition when recrystallised. The *d*-bromocamphorsulphonate crystallises as colourless prisms, m. p.  $180^\circ$  (decomp.). Attempts to resolve the salt were unsuccessful (compare Jones, *Trans.*, 1903, 83, 1417).

[With ROBERT OCHSLEN.]—*Ethyl N-methyltetrahydroquinolinium acetate d*-camphorsulphonate,  $C_{24}H_{35}O_6NS$ , prepared from the iodide, crystallises in colourless needles, decomp. about  $95^\circ$ ,  $[\alpha]_D -11$ ;  $[M]_D +51.9^\circ$ , and is hygroscopic. Attempts to resolve this salt were fruitless. G. V.

**Carbazole.** GUSTAV SCHULTZ and L. HAGENSTEIN (*J. pr. Chem.* 1907, [ii], 76, 336—349).—An investigation of the sulphonic acids of carbazole (compare Graebe and Glaser, *this Journ.*, 1872, 25, 32; Bechhold, *Abstr.*, 1890, 1297; Wirth and Schott, *Abstr.*, 1905, 1, 34).—Carbazole is sulphonated slowly at the ordinary temperature and rapidly at  $70-75^\circ$ , by concentrated sulphuric acid; the reaction product contains di- and tri-sulphonic acids together with unchanged carbazole. The disulphonic acid is isolated as the barium salt,  $C_{12}H_7N(SO_3)_2Ba \cdot 3H_2O$ , which loses  $2H_2O$  in a desiccator, and becomes anhydrous at  $180-190^\circ$ . The free acid is obtained as a transparent compact mass, m. p. below  $56^\circ$ , becomes blue on the surface, gives a brown coloration when fused with resorcinol, and on fusion with oxalic acid forms a blue dye soluble in water. The soluble  $C_{12}H_7N(SO_3Na)_2$ , and potassium salts were analysed. Carbazole disulphonyl chloride,  $C_{12}H_7N(SO_2Cl)_2$ , prepared by heating the potassium salt with phosphorus pentachloride in a water-bath, is hydrolysed by hot water, and reacts with ammonia, forming the disulphonamide,  $C_{12}H_7N(SO_2 \cdot NH_2)_2$ , which crystallises in colourless needles or triangular plates, m. p.  $220-225^\circ$ . The sulphonic groups of carbazolesulphonic acid are displaced only with difficulty; the acid remains almost unchanged when heated with alkalis at  $200^\circ$ , but yields a phenolic product at  $300-320^\circ$ . Distillation of the potassium disulphonate with potassium ferrocyanide or cyanide leads to the formation of carbazole. When heated with concentrated nitric acid on the water-bath, the potassium disulphonate yields potassium *nitro*carbazolesulphonate, which crystallises in yellow needles.

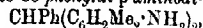
Potassium *nitro*carbazolesulphonate,  $C_{12}H_6O_2N_2(SO_3K)_2 \cdot 3H_2O$ , formed by heating potassium carbazolesulphonate with the theoretical amount of dilute nitric acid, crystallises in yellow needles, loses about  $2H_2O$  in a desiccator, becomes anhydrous at  $150^\circ$ , intumesces when heated, and dyes wool in an acid-bath a shade resembling naphthol-yellow. Reduction of the nitrodisulphonate by means of hydrogen sulphide in ammoniacal solution leads to the formation of potassium *hydrogen aminocarbazolesulphonate*,  
 $NH_2 \cdot C_{12}H_6N(SO_3K) \cdot SO_3H \cdot 3H_2O$ ,

base crystallises in colourless needles, loses  $3\text{H}_2\text{O}$  at  $120^\circ$ , and when treated with nitrous acid forms a *diazo-salt*; this couples with  $\beta$ -naphthol, forming a red dye, which crystallises in needles, and in an aqueous bath dyes wool red.

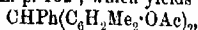
*Carbazole carbazotrisulphonate*, obtained from the filtrate from the barium disulphonate, crystallises in white needles containing  $\text{H}_2\text{O}$  which is lost at  $190$ — $195^\circ$ .

Nitration of the product of complete sulphonation of carbazole with excess of concentrated sulphuric acid on the water-bath leads to the formation of a mono- or di-nitrocarbazoledisulphonic acid, depending on the amount of nitric acid employed. The mononitro-acid is obtained in this manner in an almost quantitative yield, and, when heated and diazotised, couples with  $\beta$ -naphthol, forming a red, or with  $\alpha$ -naphthylamine a violet, dye. G. Y.

**Derivatives of *p*-Xylidine.** GUSTAV SCRULTZ and A. PETENY *Ann. Chem.*, 1907, [ii], 76, 331—336).—The base, m. p.  $208^\circ$ , obtained as a by-product in the separation of *p*- and *m*-xylidine by means of acetaldehyde is found to be *phenyldi-p-aminodi-p-xylidimethane*,



is best prepared by boiling benzaldehyde and *p*-xylidine with alcoholic hydrogen chloride. It crystallises in light yellow prisms, forms a *diacetyl* derivative,  $\text{C}_{27}\text{H}_{30}\text{O}_2\text{N}_4$ , crystallising in white needles, m. p.  $217^\circ$ , and a *dibenzoyl* derivative,  $\text{C}_{27}\text{H}_{34}\text{O}_2\text{N}_4$ , m. p.  $220$ — $230^\circ$ . The action of nitrous acid on the base leads to the formation of a *phenol*, m. p.  $162^\circ$ , which yields a *diacetate*,



crystallising in white needles, m. p.  $158^\circ$ .

Similar bases are obtained by boiling *m*- and *p*-nitrobenzaldehyde with *p*-xylidine and alcoholic hydrogen chloride.

The *m*-nitro-compound,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\text{Me}_2\text{NH}_2)_2\cdot\text{C}_6\text{H}_5$ , crystallises from benzene in yellow needles, m. p.  $216^\circ$ , and loses  $\text{C}_6\text{H}_5$  at  $100^\circ$ , forming orange needles, m. p.  $227^\circ$ . The *diacetyl* derivative,  $\text{H}\cdot\text{C}_4\text{N}_2$ , crystallises in yellow needles, m. p.  $232^\circ$ ; the *dibenzoyl* derivative,  $\text{C}_6\text{H}_5\cdot\text{O}_2\text{N}_2$ , crystallises in needles, m. p.  $261$ — $262^\circ$ . The *dichloride* was analysed.

The *p*-nitro-compound crystallises in prisms, m. p.  $162^\circ$ , or after losing  $\text{H}_2\text{O}$  at  $120^\circ$ , m. p.  $237^\circ$ . The *diacetyl* derivative crystallises in white needles, m. p.  $192^\circ$ ; the *dibenzoyl* derivative forms yellow needles, m. p.  $258$ — $259^\circ$ ; the *dihydrochloride* crystallises in yellow leaflets.

G. Y.

**Magnesium Alkylhalides and Carbodi-imides.** MAX BUSCH and ERHARD HOBEIN (*Ber.*, 1907, 40, 4296—4298).—Carbodi-imides form additive compounds with magnesium alkylhalides which are decomposed normally by water, forming amidines. Thus carbodi-imide and magnesium methyl iodide form colourless needles, m. p.  $132^\circ$ , of diphenylethenylamidine,  $\text{NHPh}\cdot\text{CMe}\cdot\text{NPh}$ . *Diphenylethenylamidine*,  $\text{NHPh}\cdot\text{CPh}\cdot\text{NPh}$ , forms colourless needles, m. p.  $41^\circ$ . Diphenyl- $\alpha$ -naphthenylamidine,  $\text{NHPh}\cdot\text{C}(\text{C}_{10}\text{H}_7)\cdot\text{NPh}$  (Büssneck, *Ber.*, 1883, 595), forms silky, glistening needles, m. p.  $184^\circ$ ; the


hydrochloride forms transparent, pointed crystals, m. p. 232°. Phenyl cyanamide and magnesium phenyl bromide form pberylphenyl amidine,  $\text{NHPh}\cdot\text{CPh}\cdot\text{NH}$ , colourless needles, m. p. 112°. E. F. A.

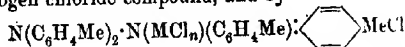
**Preparation of the Leuco-derivatives of the Indophenols.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 184601, 184651).—When the quinonemonoimines, obtained by oxidation of *p*-aminophenol and its derivatives, are condensed with aromatic bases in dilute hydrochloric acid, leuco-derivatives of the indophenols are produced, providing that the imine is not present in excess.

*p*-Aminophenol hydrochloride, when oxidised in aqueous solution with the calculated amount of ferric chloride, yields quinoneimine, and the addition of a solution of  $\alpha$ -naphthylamine hydrochloride leads to the precipitation of leucoindophenol. A similar result is obtained with *o*-chloro-*p*-aminophenol and  $\alpha$ -naphthylamine, or the sulphonic acids of this base may be employed.

The leucoindophenols are likewise produced when the phenols, having a free para-position, react with the quinonediimines in molecular proportions. Thus *s-p*-phenylenedimethyldiamine, oxidised with ferric chloride to quinonedimethylimine and then condensed with phenol in aqueous solutions, furnishes a leucoindophenol which is obtained by salting out. G. T. M.

**Tertiary Aromatic Hydrazines and Amines.** III. HEINRICH WIELAND (*Ber.*, 1907, 40, 4260–4281. Compare Abstr., 1907, i, 453, 830).—The blue or violet coloration obtained when tetraphenylhydrazine is treated with acids (Abstr., 1906, i, 453) is found to be due to the formation of salts of the hydrazine derivative. As tetraphenylhydrazine rapidly undergoes the benzidine rearrangement, the author has investigated the formation of the above salts with tetra-*p*-tolylhydrazine. These violet salts are obtained by the addition not only of acids, but also of the halogens and of halogen compounds, such as phosphorus pentachloride, thionyl chloride, antimony pentachloride, and stannic, ferric, aluminium, and zinc chlorides. These salts are additive compounds, but not double salts, and are resolved by water or alkali into the tetra-*p*-tolylhydrazine and the decomposition products of the halogen compound employed.

The structure of these additive derivatives is regarded as expressed by the formula:  $\text{N}(\text{C}_6\text{H}_4\text{Me})_2\cdot\text{NCl}(\text{C}_6\text{H}_4\text{Me})\cdot$    $\text{HMe}$  for the hydrogen chloride compound, and by

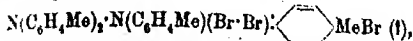


for the other halogen compounds,  $\text{MCl}_n$  representing  $\text{PCl}_5$ ,  $\text{FeCl}_3$ , &c. This quinonoid constitution is supported by the observation that tetraphenylhydrazine exhibits a tendency to form these additive derivatives much less marked than with tetra-*p*-tolylhydrazine, since, in the case of the simple quinols, the presence of a methyl group in the para-position greatly enhances the stability of the quinol form.

The reduction of these violet salts by stannous chloride yields di-*p*-tolylamine. Their spontaneous decomposition in solution also

fields di-*p*-tolylamine together with a pale red compound, which melts at a high temperature, and has the empirical composition of a diacid derivative of di-*p*-tolylamine, although it does not appear to have the simple molecular weight.

The addition of bromine to tetra-*p*-tolylhydrazine results in the formation of a perbromide,

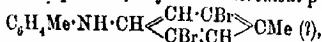


which decomposes into di-*p*-tolylamine and a dibromodi-*p*-tolylamine.

In its unchanged form, tetra-*p*-tolylhydrazine takes up 5 atoms of diac, yielding a periodide, which has the colour of the associated diac and shows none of the reactions characterising the violet diac.

Pure, colourless triphenylamine, when added to sulphuric acid either alone or in acetic acid solution, gives no coloration if the liquid is kept cool, but, on heating, an intense, blue coloration appears (compare Goldberg and Nimerovsky, this vol., i, 621); no compound analogous to those formed by tetra-*p*-tolylhydrazine is, however, obtained. Further, tri-*p*-tolylamine does not react with sulphuric, hydrochloric, or acetic acid, but gives with antimony pentachloride, bromine, or phosphorus pentachloride dark blue, crystalline, additive products, which, on decomposition, yield tri-*p*-tolylamine.

The perbromide of tetra-*p*-tolylhydrazine,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{Br}_3$ , separates from a benzene-chloroform solution in moderately stable, blackish-violet needles having a faint green, metallic lustre, and decomposes at about 58°. On decomposition, it yields a dibromodi-*p*-tolylamine,



separating from methyl alcohol in colourless, spear-like crystals, m. p. 59°.

The compound,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{PCl}_3$ , prepared from tetra-*p*-tolylhydrazine and phosphorus pentachloride, separates in slender needles. The antimony pentachloride compound,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{SbCl}_3$ , forms stable, broad needles with an intense green reflection, m. p. 107° (decomp.); the addition of pyridine to the violet solution causes the gradual disappearance of the colour, whilst the subsequent addition of water precipitates the violet compound. The periodide,  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{I}_3$ , crystallises from benzene in shining, blue scales decomposing at 113°.

Tri-*p*-tolylamine,  $\text{C}_{21}\text{H}_{21}\text{N}$ , prepared by the interaction of di-*p*-tolylamine, p-tolotoluene, and potassium carbonate in presence of copper (compare Goldberg, Abstr., 1906, i, 426), separates from acetic acid as a faintly yellow, crystalline crust, m. p. 117°, and distils undecomposed; with concentrated sulphuric acid, it gives a colourless solution, which, when heated, assumes a bluish-green colour. With bromine, it gives an unstable compound separating in dark blue, bronzy needles, m. p. 40° (decomp.), and giving a dibromotri-*p*-tolylamine, m. p. 160–165°, on decomposition. With phosphorus pentachloride, it forms a compound,  $\text{C}_{21}\text{H}_{21}\text{N} \cdot \text{PCl}_3$ , crystallising in dark blue needles, and with antimony pentachloride the compound,  $\text{C}_{21}\text{H}_{21}\text{N} \cdot \text{SbCl}_3$ , crystallising in broad, dark blue needles having a metallic lustre, m. p. 116° (decomp.).

T. H. P.

**Action of Hydrazine Hydrate on Nitro-compounds.**  
**Action of Hydrazine Hydrate on 2:4-Dinitrobenzoic Acid.**  
 THEODOR CURTIUS and HERMANN F. BOLLENBACH [and, in part, HANS CLEMM] (*J. pr. Chem.*, 1907, [ii], 78, 281—301. Compare also vol. i, 969, 970).—The action of fuming nitric acid on *p*-nitrobenzoic acid leads to the formation of a mixture of 2:4- and 3:4-dinitrobenzoic acid. 2:4-Dinitrobenzoic acid is best prepared by oxidation of 2:4-dinitrotoluene with chromic acid in concentrated sulphuric solution at 45—50°. Ethyl 2:4-dinitrobenzoate, prepared by boiling the acid with alcoholic hydrogen chloride or by the action of ethyl iodide on the silver salt, crystallises in white needles, m. p. 41°, and readily changes into an oily modification.

2-Nitro-4-aminobenzoic acid,  $C_6H_4O_4N_2$ , prepared by boiling 2:4-dinitrobenzoic acid with hydrazine hydrate in alcoholic solution, crystallises in scarlet needles, m. p. 255°. The silver,  $C_6H_4O_4N_2Ag$ , and sodium,  $C_6H_4O_4N_2Na \cdot 2H_2O$ , salts were analysed. The ethyl ester, formed by boiling ethyl 2:4-dinitrobenzoate with alcoholic hydrazine hydrate, crystallises in yellow needles, m. p. 130°, and is hydrolysed by boiling dilute sodium hydroxide, forming 2-nitro-4-aminobenzoic acid.

2-Nitro-4-aminobenzoylhydrazide,  $NO_2 \cdot C_6H_3(NH_2) \cdot CO \cdot NH \cdot NH_2$ , is formed by boiling ethyl 2-nitro-4-aminobenzoate with dilute hydrazine hydrate; it crystallises in golden leaflets or reddish-yellow columns, m. p. 212°, and reduces ammoniacal silver nitrate or Fehling's solution when heated. The benzylidene derivative,  $C_{14}H_{12}O_4N_4$ , forms yellow crystals, m. p. 187—189°; the *o*-hydroxybenzylidene derivative,  $C_{14}H_{10}O_4N_4$ , separates from alcohol in glistening crystals, m. p. 210°; the isopropylidene derivative,  $C_{10}H_{12}O_4N_4$ , forms golden crystals, m. p. 204—206°. The dibenzoyl derivative,  $NHBz \cdot C_6H_3(NO_2) \cdot CO \cdot NH \cdot NHBz$ , m. p. 239—241°, is prepared by shaking the hydrazide with benzoyl chloride in aqueous sodium hydroxide solution. The triacetyl derivative,  $C_{18}H_{14}O_7N_4$ , obtained by boiling the hydrazide with acetic anhydride, crystallises in leaflets, m. p. 255°.

Bis-2-nitro-4-aminobenzoylhydrazide,  $N_2H_2[CO \cdot C_6H_3(NH_2) \cdot NO_2]_2$ , formed by boiling the monohydrazide with alcoholic iodine solution or, together with ethyl 2-nitro-4-aminobenzoate, by the action of hydrazine hydrate on ethyl 2:4-dinitrobenzoate in ethereal or concentrated alcoholic solution, separates from aqueous alcohol in yellowish-brown crystals, m. p. 238°, and when heated with alcoholic hydrogen chloride at 110° yields hydrazine and 2-nitro-4-aminobenzoic acid.

2-Nitro-4-aminobenzoylazoimide,  $NO_2 \cdot C_6H_3(NH_2) \cdot CO \cdot N_2$ , prepared by the action of sodium nitrite on the hydrazide in acetic acid solution, is obtained as an unstable, red, flocculent precipitate, detonates when heated on platinum, is hydrolysed by dilute sodium hydroxide, forming azoimide and sodium 2-nitro-4-aminobenzoate, and is converted by boiling aniline into 2-nitro-4-aminobenzanilide,  $C_{13}H_{11}O_2N_3$ , which crystallises in white needles, m. p. 226°, and forms an acetyl derivative  $NHAc \cdot C_6H_3(NO_2) \cdot CO \cdot NHPh$ , crystallising in yellow needles, m. p. 238°. The action of boiling alcohol on the azoimide leads to the formation of a dark red syrup, which is probably 2-nitro-4-aminophenylurethane,  $NO_2 \cdot C_6H_3(NH_2) \cdot NH \cdot CO_2Et$ , since, on successive treatment with an alkali and hydrochloric acid, it yields nitro-*p*-phenylene

amine. When boiled with water the acidimide forms hydrazine and *bis*-2-amino-4-nitrophenylcarbamide.



which is hydrolysed by prolonged boiling with concentrated sodium hydroxide, forming nitro-*p*-phenylenediamine.

Experimental details as to the action of hydrazine hydrate on nitrobenzene, *m*-dinitrobenzene, nitrophenols, *m*- and *p*-nitrobenzoic acids, and *p*-nitrosodimethylaniline are now given (compare this vol. 1, 163).

G. Y.

**Action of Hydrazine Hydrate on Nitro-compounds. IV.**  
**4-Nitro- and 4-Amino-phthalhydrazides.** THEODOR CURTIUS and ALFRED HOESCH (*J. pr. Chem.*, 1907, [ii], 76, 301—330. Compare this vol. 969, 970, and preceding abstract).—When boiled with alcoholic hydrazine hydrate, ethyl 4-nitrophthalate forms *hydrazonium*

4-nitrophthalylhydrazide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{N} \cdot \text{N}_2\text{H}_5$ , which is obtained in

yellow and red modifications, does not melt at 300°, forms a red aqueous solution, yields benzaldazine when shaken with aqueous benzaldehyde, and, on treatment with acetic acid, yields 4-nitrophthalylhydrazide (Bogert and Boroschek, *Abstr.*, 1902, i, 98). This is obtained in golden plates, m. p. 298°, sublimes slowly at 200°, has an acid reaction in aqueous solution, and dissolves in aqueous alkalis or alkali carbonates, forming a deep red solution which gives precipitates with salts of the heavy metals. The *potassium*,  $\text{C}_6\text{H}_3\text{O}_5\text{N}_4\text{K}_3$ , *sodium*,  $\text{C}_6\text{H}_3\text{O}_5\text{N}_4\text{Na}_3$ , and *copper*,  $\text{C}_6\text{H}_3\text{O}_5\text{N}_4\text{Cu}$ , salts are described. The hydrazide remains unchanged when boiled with benzaldehyde or bromine and acetic acid, but yields hydrazine and  $\beta$ -nitrophthalic acid when heated with concentrated hydrochloric acid at 150°. The

*methyl* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NMe}$ , prepared by heating the

potassium salt with methyl iodide at 150°, crystallises in yellow needles, m. p. 295°, and dissolves in aqueous alkalis, forming a red

solution. The *diacetyl* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{N}(\text{Ac})_2$ , obtained by

heating the hydrazide with acetic anhydride, forms white leaflets, m. p. 165°, and is hydrolysed by boiling water. *Ethyl* 4-nitrophthalyl-

hydrazidecarboxylate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{N} \cdot \text{CO}_2\text{Et}$ , formed by heating

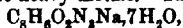
the potassium salt with ethyl chlorocarbonate, crystallises in yellow leaflets, m. p. 115°, and is hydrolysed by boiling water, yielding the hydrazide. The action of ethyl chloroacetate on the potassium salt at

120—156° leads to the formation of a red powder,  $\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}_4$ , m. p. 182°. 4-Nitrophthalylhydrazide is attacked by fuming nitric acid at -10°, but not by concentrated nitric acid at the ordinary temperature; the action of potassium permanganate, chromic acid, or potassium dichromate and concentrated sulphuric acid leads to the formation of 4-nitrophthalic acid.

**4-Aminophthalylhydrazide**,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}$ , prepared by the re-



duction of the micro-organisms with hydrazine, or by heating the nitro-hydrazide with an excess of hydrazine hydrate at 130–140°, crystallises in yellow, microscopic needles, does not melt at 300°, has an acid reaction in aqueous solution, is precipitated from its brown alkaline solutions by carbon dioxide, dissolves in hot dilute acids, but separates unchanged on cooling, and gives precipitates with salts of the heavy metals. The sodium,



calcium,  $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_2\text{Ca}$ , and copper,  $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_2\text{Cu}$  and  $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Cu}\cdot\text{OH}$  salts are described. When heated with concentrated hydrochloric acid at 150°, the hydrazide is hydrolysed, forming hydrazine and 4-aminophthalic acid; oxidation with nitric acid, permanganate, or dichromate leads to the complete destruction of the molecule. The

ethyl derivative,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NEt} \end{smallmatrix}$ , formed from the sodium salt, separates from water in flocculent crystals, m. p. 155°. The diacetyl

derivative,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NAc} \end{smallmatrix}$ , crystallises in yellow plates, m. p.

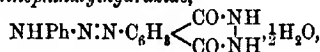
212°, and when boiled with water yields a white mixture of the mono- and di-acetyl derivatives, m. p. about 270°. Ethyl 4-aminophthalyl-

hydrazidedicarboxylate,  $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{N}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , crystallises in yellow leaflets, m. p. 148–150°.

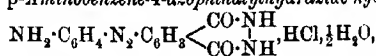
Diazotisation of 4-aminophthalhydrazide with sodium nitrite in sulphuric acid solution leads to the formation of a dark red solution, which, when heated on the water-bath, evolves nitrogen, and, on cooling,

deposits 4-hydroxyphthalylhydrazide,  $\text{OH}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ ; this forms an amorphous, yellow powder, does not melt at 300°, and dissolves in aqueous alkalis or alkali carbonates to a yellowish-red solution. The diazo-sulphate solution couples with resorcinol in alkaline solution, forming a red dye,  $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_4$ , which in alkaline solution dyes vegetable and animal fibres yellow.

*Benzenediazoaminophthalylhydrazide,*



formed by the action of sodium acetate on a mixture of aniline hydrochloride and diazotised 4-aminophthalylhydrazide in hydrochloric acid solution, is obtained as a yellow precipitate, m. p. 185–187°, and evolves a gas and yields an odour of phenol when heated with dilute acids. *p-Aminobenzene-4-azophthalylhydrazide hydrochloride,*



formed by heating the preceding substance with aniline and aniline hydrochloride, crystallises in dark red prisms, m. p. about 240°, and, when treated with carbon dioxide in ammoniacal solution, yields the free base,  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_6$ , which is obtained as an amorphous powder, does not melt at 300°, and is soluble in acids and alkalis. G. Y.

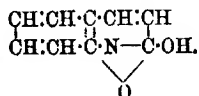
**Synthesis of Quinoline Derivatives. IV. Action of Ethyl Benzoylacetate on Anthranilic Acid.** STEFAN VON NISSENGROWSKI (*Ber.*, 1907, 40, 4285—4294. Compare *Abstr.*, 1905, i, 611).—The compound,  $C_{22}H_{20}O_4N_2$ , m. p.  $308^\circ$  [ $1318^\circ$ ]; described previously (*loc. cit.*) as a by-product of the interaction of ethyl benzoylacetate (1 mol.) and anthranilic acid (1 mol.), is shown to be 4-anilino-2-hydroxyquinoline,  $C_{15}H_{13}ON$ , which is obtained in better yield by the action of 2 mols. of anthranilic acid on 1 mol. of the ester. It crystallises from acetone, methyl alcohol (+ Me·OH), or acetic acid or anhydride (+  $C_2H_4O_2$ ) in microscopic, six-sided plates, m. p.  $318^\circ$ , and acts as a feeble, monobasic acid. Its hydrochloride,  $C_{15}H_{13}ON_2HCl$ , forms silky needles, m. p.  $160$ — $165^\circ$ . By the action of fused potassium or sodium hydroxide, or by heating with hydrochloric acid in a sealed tube, 4-anilino-2-hydroxyquinoline is resolved into aniline and 4-hydroxycarbostyryl (2:4-dihydroxyquinoline). The latter compound, when obtained from its sodium derivative and acetic acid, separates as a crystalline powder, m. p.  $340$ — $344^\circ$ , whilst, after long boiling with nitrobenzene or aniline, it forms stout crystals, m. p.  $355^\circ$ .

When distilled with zinc dust under very low pressure, 4-anilino-2-hydroxyquinoline yields 4-anilinoquinoline (compare Ephraim, *Abstr.*, 1893, i, 727).

2-Chloro-4-anilinoquinoline,  $C_{15}H_{11}N_2Cl$ , obtained by the action of phosphorus pentachloride and oxychloride on 4-anilino-2-hydroxyquinoline, crystallises from alcohol in concentric groups of white needles, m. p.  $156^\circ$ , forms a yellow hydrochloride, m. p.  $247^\circ$ , and, when boiled with excess of aniline, yields 2:4-dianilinoquinoline (Ephraim, *loc. cit.*), which separates from alcohol in rhombic crystals.

The mechanism of the formation of 4-anilino-2-hydroxyquinoline is probably as follows. One of the two mols. of anthranilic acid is resolved into carbon dioxide and aniline, the latter then immediately reacting with the second mol. of anthranilic acid giving aminobenzoyl-anilide. This then reacts either with ethyl benzoylacetate yielding 4-anilino-2-hydroxy-3-benzoylquinoline, the benzoyl group of which is removed by hydrolysis, or with ethyl acetate, a product of the decomposition of ethyl benzoylacetate, giving 4-anilino-2-hydroxyquinoline directly.

The compound,  $C_9H_7O_2N$ , termed hydroxycarbostyryl by Friedländer and Ostermaier (*Abstr.*, 1882, 201, 732), and obtained together with carbostyryl by reducing ethyl o-nitrocinnamate with alcoholic ammonium sulphide, is regarded by the author as having the constitution:



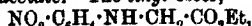
T. H. P.

**Preparation of 5-Hydroxy-3'-aminophenyl-1:2-naphth-iminazoledisulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 186883).—5-Hydroxy-3'-aminophenyl-1:2-naphthiminazole-7- $\beta$ -disulphonic acid is an almost colourless, sparingly

...oxy-3'-amino-4'-nitro-1,2-bis(4-nitrophenyl)-1,2-sulphonate salt on the water-bath with fuming sulphuric acid (20%  $\text{SO}_3$ ). Its alkali salts are readily soluble; the salts of sodium, potassium, and ammonium are also those of barium, strontium, and calcium; the yellow compound dissolves in water only sparingly.

G. T. M.

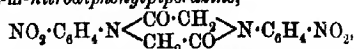
**2:6-Diketo-dinitro- and -diamino-diphenylpiperazines.** DEUTSCH (*J. pr. Chem.*, 1907, [ii], 76, 350—363).—*m*-Nitrophenylglycine,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by heating *m*-nitroaniline with chloroacetic acid in sodium acetate and carbonate solution, crystallises in doubly refracting, yellow, rhombic prisms, m. p. 150° (corr.), decomp. slightly above its m. p., and dissolves in aqueous sodium carbonate or acetate. The *ethyl ester*,



prepared from *m*-nitroaniline and ethyl chloroacetate, forms pleochroic crystals, m. p. 84° (corr.).

Chloroacetyl-*m*-nitroanilide (Johnson and Cramer, *Abstr.* 1903, 1, 161) crystallises in doubly refracting plates, m. p. 116° (corr.), decomp. 150—160°, and is hydrolysed by alcoholic potassium hydroxide, forming *m*-nitroaniline together with traces of the *m*-nitroanilide of glycollic acid if in presence of water.

**2:5-Diketodi-*m*-nitrodiphenylpiperazine,**



is obtained in a 20% yield when *m*-nitrophenylglycine, or in a 10% yield when chloroacetyl-*m*-nitroanilide, is heated at 160—170°; it forms a yellow, crystalline powder, m. p. 157° (corr.), and is hydrolysed to *m*-nitrophenylglycine by alcoholic potassium hydroxide.

The action of chloroacetyl chloride on *m*-nitrophenylglycine leads to the formation of *chloroacetyl-m-nitrophenylglycine*, which cannot be obtained free from unchanged *m*-nitrophenylglycine; when boiled with excess of *m*-nitroaniline in benzene, it forms small amounts of 2:5-diketodi-*m*-nitrodiphenylpiperazine. Reduction of this with tin and hydrochloric acid leads to the formation of 2:5-diketo-*di-m*-amino-diphenylpiperazine dihydrochloride,  $\text{C}_{16}\text{H}_{18}\text{O}_6\text{N}_4\text{Cl}_2$ , which is obtained in colourless, doubly refracting crystals. The free base is colourless, but on exposure to air rapidly becomes yellow, changing to green and black. Orange-red to yellow dyes, which dye wool, but not cotton, are obtained by coupling the diazotised base with R-salt and salicylic acid.

Chloroacetyl-*p*-nitroanilide crystallises in doubly refracting plates, m. p. 152° (corr.), and resembles the *m*-nitroanilide in its behaviour with hydrolysing agents. When heated at 170°, it yields 2:5-diketodi-*p*-nitrodiphenylpiperazine,  $\text{C}_{16}\text{H}_{18}\text{O}_6\text{N}_4$ , which is obtained as a yellow powder, m. p. 147° (corr.), and when boiled with alcoholic potassium hydroxide is hydrolysed to *p*-nitrophenylglycine. The dihydrochloride, obtained on reduction of the di-*p*-nitro-compound in hydrochloric acid solution, forms colourless, doubly refracting prisms; the free base is colourless, rapidly darkens on exposure to air, and, when diazotised and coupled with R-salt and salicylic acid, yields dyes which dye wool but not cotton, a dirty, brown yellow.

G. Y.

# Pyrimidines

acid. HENRY L. WHEELER and CARL O. JOHNS (Amer. Chem. Soc., 1907, 29, 594-602).—When ethyl 2-ethylthiol-6-oxypyrimidine-5-carboxylate (Wheeler, Johnson, and Johns, this vol., i, 559) is treated with phosphorus oxychloride, it is converted into ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate, 
$$\text{N} \begin{array}{c} \text{C(SEt)} \\ \text{C} \\ \text{C} \end{array} \begin{array}{c} \text{N} \\ \text{C} \\ \text{C} \end{array} \text{CH, b. p. 103-104/20 mm.} \text{ This substance, on treatment with cold alcoholic ammonia, yields ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate, } \text{N} \begin{array}{c} \text{C(SEt)} \\ \text{C} \\ \text{C} \end{array} \begin{array}{c} \text{N} \\ \text{C} \\ \text{C} \end{array} \text{CH, m. p. 102}^\circ, \text{ which forms rectangular plates; the corresponding acid, m. p. 230}^\circ \text{ (decomp.), crystallises in microscopic prisms, and when heated with concentrated hydrochloric acid is converted into cytosine-5-carboxylic acid,}$$

$$\text{N} \begin{array}{c} \text{CO} \\ \text{C} \\ \text{C} \end{array} \begin{array}{c} \text{NH} \\ \text{C} \\ \text{C} \end{array} \text{CH,}$$
  
 m. p. 256-257° (decomp.). The hydrochloride of cytosine-5-carboxylic acid, m. p. 275-276°, forms pointed prisms containing 1H<sub>2</sub>O. The ethyl ester crystallises in needles, and decomposes slowly at 260-270°. The amide forms tufts of hair-like needles. When cytosine-5-carboxylic acid is heated with 20% sulphuric acid, it yields uracil-5-carboxylic acid (*loc. cit.*) together with a small quantity of cytosine. These results indicate that cytosine does not exist in the nucleic acids in the form of a 5-carboxyl derivative.

Ethyl 2,6-diaminopyrimidine-5-carboxylate, 
$$\text{N} \begin{array}{c} \text{C(NH}_2\text{)} \\ \text{C} \\ \text{C} \end{array} \begin{array}{c} \text{N} \\ \text{C} \\ \text{C} \end{array} \text{CH,}$$
  
 m. p. 205-207°, obtained by heating ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate with alcoholic ammonia at 168-175°. E. G. crystallises in needles.

Pyrimidines. XXVII. Synthesis of Thymine-5'-carboxylic Acid. TREAT B. JOHNSON and CARL FRANK SPER (Amer. Chem. J., 1907, 38, 602-613).—The study of the carboxylic acids of uracil, cytosine, and thymine has been undertaken with a view to obtain evidence as to whether these bases are linked in nucleic acid by means of an acid amide group (compare Wheeler, Johnson, and Johns, this vol., i, 559, and preceding abstract; Johnson, this vol., i, 879, and Wheeler, this vol., i, 972). The results so far obtained indicate that uracil is the only one of these pyrimidines which is capable of being united in this way and that this might exist as a 5-carboxyl compound.

Ethyl formylsuccinate, CO<sub>2</sub>Et·CH(CHO)·CH<sub>2</sub>·CO<sub>2</sub>Et, b. p. 158-160°/20 mm., is obtained by the condensation of ethyl formate and succinate in presence of sodium. By the action of its sodium derivative on ψ-ethylthiocarbamide, ethyl 6-oxy-2-ethylthiopyrimidine-5-acetate, 
$$\text{NH} \begin{array}{c} \text{C(SEt)} \\ \text{C} \\ \text{C} \end{array} \begin{array}{c} \text{N} \\ \text{C} \\ \text{C} \end{array} \text{CH, m. p. 146-147}^\circ, \text{ is produced which forms slender needles. The corresponding acid, m. p. 184}^\circ, \text{ crystallises in needles and square plates; its potassium salt forms long needles.}$$

By the action of phosphorus oxychloride on ethyl 6-oxy-2-ethyl-

thiopyrimidine-5-acetate, 4-chloro-2-ethylthiopyrimidine-5-acetic acid  $\text{N} \begin{array}{c} \text{C(SEt)} \\ \text{C(SeEt)} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \begin{array}{c} \text{C(SeEt)} \\ \text{C(SeEt)} \end{array} \text{CH}_2 \cdot \text{CO}_2\text{H} \rangle \text{CH}$ , m. p.  $132^\circ$ , is produced and forms clusters of prismatic crystals. The corresponding amide, m. p.  $214^\circ$  (decomp.), obtained by heating ethyl 6-oxy-2-ethylthiopyrimidine-4-acetate with alcoholic ammonia at  $140-150^\circ$ , crystallises in prismatic needles; if the mixture is heated at  $170-180^\circ$ , 2-amino-6-oxypyrimidine-5-acetamide,  $\text{NH} \begin{array}{c} \text{C(NH}_2) \\ \text{C(NH}_2) \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \begin{array}{c} \text{C(NH}_2) \\ \text{C(NH}_2) \end{array} \text{CH}_2 \cdot \text{CO}_2\text{NH}_2 \rangle \text{CH}$ , is produced which forms prismatic crystals and decomposes at about  $280^\circ$ .

Thymine- $\omega$ -carboxylic acid,  $\text{NH} \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \text{CH}_2 \cdot \text{CO}_2\text{H} \rangle \text{CH}$ , m. p.  $315-320^\circ$  (decomp.), obtained by the action of hydrochloric acid on ethyl 2-ethylthiol-6-oxypyrimidine-5-acetate, forms microscopic granular crystals, dissolves to the extent of 0.35–0.40 part in 100 parts of water at  $30^\circ$ , reddens blue litmus, and yields a precipitate with solutions of silver nitrate or mercuric chloride. The potassium and lead salts are described. The ethyl ester, m. p.  $204-219^\circ$ , forms rectangular plates. The acid can be heated with 20% sulphuric acid without change, and it therefore follows that thymine cannot exist in nucleic acids as a  $\omega$ -carboxyl compound. E. G.

Preparation of 5:5-Dialkylbarbituric Acids. FARBENFABRIK VORM. FRIEDR. BAYER & Co. (D.R.-P. 180669. Compare Abstr., 1905, i, 671).—The 2:4-di-imino-6-oxy-5:5-dialkylpyrimidines when heated with mineral acids readily lose their two imino-groups and yield the corresponding 5:5-dialkylbarbituric acids. In this way, 2:4-di-imino-6-oxy-5:5-diethylpyrimidine gives rise to 5:5-diethylbarbituric acid, and 2:4-di-imino-6-oxy-5:5-dimethylpyrimidine furnishes 5:5-dimethylbarbituric acid, small leaflets, m. p.  $267^\circ$ . G. T. M.

Pyrazolone Derivatives. RUDOLF KOBERT (*Chem. Zentr.*, 1907, i, 1804–1805; from *Zeitsch. klin. Med.*, 1907, 62, 1–43. Compare Michaelis, this vol., i, 246).—The behaviour of antipyrine, 3-antipyrine, isantipyrine, nitroso- and amino-antipyrines, pyrazolidone, 3-pyrazolidone, pyrazolidone methiodide, isopyrazolidone, and thiopyrazolidone towards several reagents is given in the original. The physiological action of several of these compounds has also been investigated. Toxicity decreases in the order: 3-antipyrine, isantipyrine, antipyrine, and aminoantipyrine. Pyrazolidone is more poisonous than isopyrazolidone, 3-pyrazolidone, 3-pyrazolidone methiodide, and aminoantipyrine. Azoantipyrine and 4-alkylantipyrine are also very poisonous. W. H. G.

Colouring Matters of the Indanthrene Series. FARBENFABRIK VORM. FRIEDR. BAYER & Co. (D.R.-P. 178130).—The 1:2- and 2:5-diaminoanthraquinones condense with alizarin and its derivatives to yield indanthrene colouring matters containing two anthraquinone residues; the condensation being generally effected by heating the reagents in boiling phenol or cresol in the presence of boric acid. The indanthrene obtained from 1:2-diaminoanthraquinone and alizarin

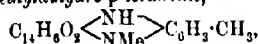
in the formula:  $\text{C}_6\text{H}_5\text{--}\langle\text{CO}\rangle\text{--}\text{C}_6\text{H}_5\text{--}\langle\text{NH}\rangle\text{--}\text{C}_6\text{H}_5\text{--}\langle\text{CO}\rangle\text{--}\text{C}_6\text{H}_5$ , and is stably isomeric with the indanthrene of commerce.

Purpurin and 1:2-diaminoanthraquinone gives rise to hydroxy-danthrene, which, on reduction, yields a blue vat-dye and gives various blue shades on unmordanted cotton. The patent contains a tabulated description of nine of these indanthrene derivatives.

G. T. M.

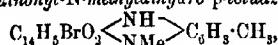
[Preparation of Azines Derived from Anthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 184391).—

When the aldehydes react with the aryl-o-diaminoanthraquinones, the coloured substances are produced, which are regarded as azine derivatives. 2-Amino-1-p-tolylaminoanthraquinone, when condensed with formaldehyde solution (40%) in glacial acetic acid at 100°, furnishes anthraquinonyl-N-methyl-dihydro-p-toluzine,



which separates as a blue, crystalline precipitate.

3-Bromoanthraquinonyl-N-methyl-dihydro-p-toluzine,



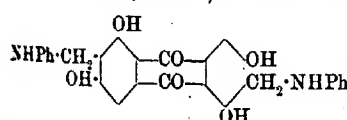
in the form of blue needles, is prepared in a similar manner from 3-bromo-2-amino-p-tolylaminoanthraquinone. The properties of these and seven other complex dihydro-azines are tabulated in the patent. The sulphonics of all these substances are wool dyes, giving various shades of blue.

G. T. M.

[Preparation of 2':2'-Dianthraquinonyl-1:5-diaminoanthraquinone.] BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 184905).—When 1:5-diaminoanthraquinone is heated to boiling in naphthalene or nitrobenzene solution with 2-chloroanthraquinone in the presence of dry sodium acetate and cupric or cuprous chloride, 2':2'-dianthraquinonyl-1:5-diaminoanthraquinone,  $\text{C}_{10}\text{H}_6\text{O}_2(\text{NH}\text{--}\text{C}_{10}\text{H}_7\text{O}_2)_2$ , is produced as a compound insoluble in the organic media; it dissolves in concentrated sulphuric acid to a green solution, and is reduced by alkaline hyposulphite to give a vat-dye producing very fast shades of red on cotton.

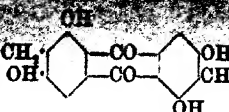
G. T. M.

[Preparation of  $\omega$ -Dianilinodimethyltetrahydroxyanthraquinone and *pp*-Tetramethyldiaminodibenzyltetrahydroxyanthraquinone.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 184807, 184808).—The condensation product from anthra-



chrysone (tetrahydroanthraquinone) and formaldehyde, when heated with excess of aniline so long as steam is evolved, gives rise to  $\omega$ -dianilino-2:4:6:8-

tetrahydro-3:7-dimethylantraquinone, separating from the cooled

$\text{Me}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ 

 $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2$

ylindines. pp-Tetramethyldiamino-2:4:6:8-tetrahydroxy-3:7-dimethoxyanthraquinone, produced by substituting dimethylaniline for aniline in the foregoing condensation, separates in orange-yellow crystals, m. 272°. The corresponding tetraethyl derivative melts at 232°.

G. T. Y.  
**Oxadiazines.** II. OTTO DIELS and ERICH SASSE (*Ber.*, 1907, 4052—4059. Compare Abstr., 1905, i, 946).—*iso*-Nitrosoacetophenone and *syn*-benzaloxime react like diacetylmonoxime with *syn*-benzaloxime hydrochloride forming oxadiazines. In the presence of anhydrous hydrogen chloride, the *isonitroso*-compound reacts with itself (or with its isomeric modification) yielding an oxadiazine containing a carbonyl group, from which an oxime is readily obtained. Thus from *isonitrosoacetophenone* is obtained an oxime of the formula  $\text{C}_8\text{H}_7\text{O}_3\text{N}_2$ , which appears to be identical with a substance prepared by Müller and von Pechmann (Abstr., 1890, 51) and by Scholl (Abstr., 1891, 287). The latter regarded the substance as the dioxime of 5-benzoyl-3-phenyl-4-*isooxazolone*. The author brings forward evidence to show that the preparation and properties of the substance harmonize better with the oxadiazine formula,  $\text{O} \begin{smallmatrix} \text{N} \\ \text{C}(\text{CPh:NOH}) \end{smallmatrix} \text{CH} \text{N} \text{CPhOH}$ .

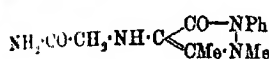
4-Hydroxy-6-phenyl-4-methyl-1:2:5-oxadiazine,  
 $\text{O} \begin{smallmatrix} \text{CPh:N} \\ \text{N=CH} \end{smallmatrix} \text{CMeOH}$ ,  
 darkens at 170—180° and decomposes at 220—225°; the methiodide  $\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_2\text{I}_2$ , has m. p. 108—109°. The hydrochloride,  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2\text{HCl}$ , m. p. 137—138°, softening at 134—135°, is prepared from *isonitrosoacetophenone* and *syn*-benzaloxime hydrochloride in methyl-alcohol solution; with boiling water, it yields the preceding base.

4-Hydroxy-6-benzoyl-4-phenyl-1:2:5-oxadiazine hydrochloride,  $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2\text{HCl}$ , is obtained by passing a rapid current of hydrogen chloride through an ethereal solution of *isonitrosoacetophenone*; it separates in stout, yellow, prismatic needles, which decompose violently at 215°. Boiling water liberates the base,  $\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ , m. p. 220—226°, which forms a yellow, crystalline sodium salt, which decomposes at 215°, and the oxime, which decomposes at 221—222° (Müller and von Pechmann, m. p. 219°; Scholl, m. p. 207—211°). C. S.

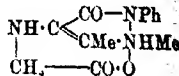
**Preparation of 4-Antipyrildimethylamine.** FARBERWERKE VON MANFRED, LUCIUS, & BRUNING (D.R.-P. 184850).—4-Cyanomethyl-1-phenyl-2:3-dimethylpyrazolone (4-antipyrilcyanomethylamine)  $\text{CH}_3\text{CH}_2\text{NH} \begin{smallmatrix} \text{CO-NPh} \\ \text{CMe-NMe} \end{smallmatrix}$ , colourless leaflets, m. p. 112°, is pro

by treating 4-antipyrilol with formaldehyde and potassium cyanide, when it separates as an oil which is solid on cooling; it dissolves only sparingly in ether, but is readily soluble in hot water or benzene, or in cold alcohol in the form of a crystalline solid.

4-Antipyrilaminocetamide (I), m. p. 194°, colourless prisms from alcohol or water, is obtained on boiling the preceding cyanide.



(I.)



(II.)

compound with water, or on leaving it in contact with concentrated hydrochloric acid. On boiling either of the preceding compounds with concentrated hydrochloric acid, the betaine (II) is reduced, which is only sparingly soluble in all organic media, and crystallises from alcohol in lustrous needles, m. p. above 300°.

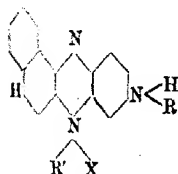
4-Antipyrilcyanodimethylamine,  $\text{CN}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{C}\begin{array}{l} \text{CO}\cdot\text{NPh} \\ \text{CMe}\cdot\text{NMe} \end{array}$ , colourless crystals, m. p. 75°, is prepared by alkylating 4-antipyrilcyanomethylamine with methyl iodide in methyl-alcoholic solution.

4-Antipyrilmethylaminocetamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{C}\begin{array}{l} \text{CO}\cdot\text{NPh} \\ \text{CMe}\cdot\text{NMe} \end{array}$ , melts from benzene, m. p. 158—159°, is similarly obtained by methylating 4-antipyrilaminocetamide.

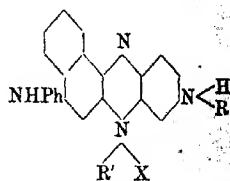
4-Antipyrilmethylaminocetic acid, prepared by methylating the foregoing betaine, is a very soluble substance, having a hygroscopic sodium salt soluble in chloroform.

The last three compounds can be hydrolysed so as to yield the therapeutically important 4-antipyrildimethylamine. G. T. M.

[Preparation of Naphthaphenosafrafranine Derivatives.]  
FRIEDRICH KEHRMANN (D.R.-P. 183117).—The isorosinduline salts of the general type (I; where X is the acid ion) have the



(I.)



(II.)

hydrogen atom, indicated in the naphthalene residue, replaced by the group  $\text{NHR}'$  when the colouring matter is treated with an amine in the presence of an oxidising agent, such as

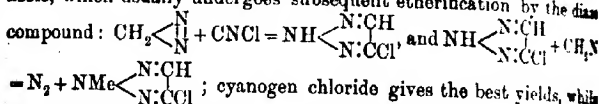


atmospheric air. Condensation with aniline would lead to the formation of substances indicated by the general formula (II).

Ethylisozosinduline chloride, obtained from nitrosoethylaniline or phenyl- $\beta$ -naphthylamine when treated with aniline and aqueous sodium hydroxide at 80–90° while a current of air is passed through the mixture, gives rise to a colour base separating in green crystals with a metallic lustre. Phenylisozosinduline chloride and *p*-aminacetanilide yield a similar product, which separates in golden-yellow crystals. Sulphonation and hydrolysis of the acetyl group lead to the production of a soluble sulphonic dye. Phenylisozosinduline chloride sulphonic acid furnishes similar condensation products on treatment with aromatic amines and sodium hydroxide.

G. T. M.

**Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives.** III. Halogenated Compounds. ANTONIO TAMBURELLO and A. MILAZZO (*Atti R. Accad. Lincei*, 1907 [v], 18, ii, 412–418. Compare Peratoner and Azzarello, this vol. i, 979).—The action of cyanogen chloride or bromide on diazomethane or diazoethane in ethereal solution yields a chloro-derivative of oxotriazole, which usually undergoes subsequent etherification by the diazo compound:



with the iodide no definite compounds were obtained.

4-Chloro-3-methylisotriazole,  $\text{NH} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagup \quad \diagdown \\ \text{N}:\text{CCl} \end{smallmatrix}$ , prepared from cyanogen chloride and diazoethane, crystallises from benzene in shining, white needles, m. p. 77–78°.

4-Chloro-3-methyl-1-ethylisotriazole,  $\text{NEt} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagup \quad \diagdown \\ \text{N}:\text{CCl} \end{smallmatrix}$ , is a colourless liquid, b. p. 86–88°/40 mm., which has a pleasing odour and is insoluble in water.

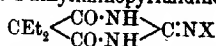
4-Bromo-3-methyl-1-ethyltriazole,  $\text{C}_5\text{H}_5\text{N}_3\text{Br}$ , is a colourless liquid, b. p. 84–85°/30 mm., having a pleasant odour.

3-Chloro-1-methylisotriazole,  $\text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ \diagup \quad \diagdown \\ \text{N}:\text{CCl} \end{smallmatrix}$ , is a colourless liquid, b. p. 62–65°/39 mm., having a pleasant odour.

3-Bromo-1-methylisotriazole,  $\text{NMe} \begin{smallmatrix} \text{N}:\text{CH} \\ \diagup \quad \diagdown \\ \text{N}:\text{CBr} \end{smallmatrix}$ , is a colourless liquid, b. p. 62–65°/22 mm., and has a pungent odour which excites to tears.

T. H. P.

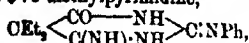
**Preparation of 2-Alkyliminopyrimidines.** EMANUEL MEXX (D.R.-P. 186456).—The 2-alkyliminopyrimidines,



where X is an alkyl or aryl group, were obtained by condensing the corresponding guanidine,  $\text{NX}:\text{C}(\text{NH}_2)_2$ , with malonyl halides, alkyl

isomates, alkyl isocyanates, or their mono- and dialkyl derivatives.

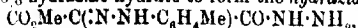
Phenylguanidine and ethyl cyanodiethylacetate give rise to 4-imino-2-phenylimino-5:5-diethylpyrimidine,



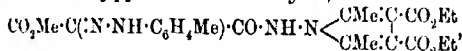
which is readily hydrolysed to 5:5-diethylbarbituric acid.

4-Imino-6-oxy-2-phenyliminopyrimidine, m. p. 244°, was produced by heating phenylguanidine and ethyl cyanoacetate with alcoholic sodium ethoxide. 4-Imino-6-oxy-2-methylimino-5:5-diethylpyrimidine, m. p. 265°, was obtained from methylguanidine and ethyl cyanodiethylacetate. 4:6-Dioxy-2-phenylimino-5:5-diethylpyrimidine, needles, m. p. 255°, was prepared from phenylguanidine and diethylmalonyl chloride. G. T. M.

**Derivatives of Methyl Mesoxalate-*p*-tolylhydrazone.** CARL FLOW and RICHARD WEIDLICH (*Ber.*, 1907, 40, 4326—4332. *Compt. Rend.*, 1906, i, 981).—Methyl mesoxalate-*p*-tolylhydrazone (Flow and Ganghofer, *Abstr.*, 1905, i, 90) in cold alcoholic solution acts with 50% hydrazine hydrate to form the hydrazide,



m. p. 160°, which separates from dilute alcohol in slender, yellow needles, and is converted by acetic anhydride into the acetyl derivative,  $\text{O} \cdot \text{Me} \cdot \text{C}(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \cdot \text{NH} \cdot \text{NHAc}$ , m. p. 186°. The hydrazide condenses with benzaldehyde in boiling alcohol to form the azylidene compound,  $\text{CO}_2\text{Me} \cdot \text{C}(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$ , m. p. 163°, and with acetone, yielding the isopropylidene compound,  $\text{CO}_2\text{Me} \cdot \text{C}(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CMe}_2$ , m. p. 55°. The hydrazide and ethyl diacetylsuccinate in very slightly diluted glacial acetic acid form methyl diethyl mesoxalyl-*p*-tolylhydrazone-amino-2:5-dimethylpyrrole-3:4-dicarboxylate,



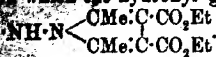
m. p. 161—162°, which separates from dilute alcohol in stout, yellow needles.

The dihydrazide,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{CO} \cdot \text{NH} \cdot \text{NH}_2)_2$ , m. p. 196°, is obtained by heating the mother liquor of the monohydrazide for five hours on the water-bath, or the calculated quantities of 50% hydrazine hydrate and methyl mesoxalate-*p*-tolylhydrazone for four hours; the dihydrazide,  $\text{C}_4\text{H}_8\text{O}_4\text{N}_6$ , m. p. 247°, is a yellow powder. Ethyl mesoxalyl-*p*-tolylhydrazone-bis-1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{N} \cdot \text{C}(\text{CO} \cdot \text{NH} \cdot \text{N} \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array})_2$ , m. p. 241°, crystallises in slender, yellow needles, and dissolves in dilute sodium hydroxide.

**3:5-Pyrazolidone-4-*p*-tolylhydrazone,**  $\text{NH} \cdot \text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{C} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , m. p. 267°, is prepared by passing carbon dioxide through the mother liquor of the dihydrazide or through the cold filtrate obtained after heating methyl mesoxalate-*p*-tolylhydrazone and a slight excess of

hydrates, m. p. 170°, which crystallise in red needles.

The authors formulate the rule: hydrazides of organic acids with ethyl diacetylsuccinate in acetic acid solution to form compounds in which the hydroxyl group of the acid is replaced by the compound



[Diazotisation of Acetyl-2:6-diaminophenol-4-sulphonic Acid.] KALLE & Co. (D.R.-P. 182853).—6-Nitro-2-acetylaminophenyl sulphonic acid is reduced without losing its acetyl group or undergoing condensation by means of iron filings and water acidified with acetic acid. The resulting acetyl-2:6-diaminophenol-4-sulphonic acid yields a very stable diazo-compound, which when warmed at 40° for six hours with dilute hydrochloric acid loses its acetyl group, while the diazo-complex remains intact.

Transformations of Azo-compounds into Hydrazones. O. DINGROTH and MAX HARTMANN (*Ber.*, 1907, 40, 4460—4465).—Benzeneazo- and *p*-bromobenzeneazo-acetyldibenzoylmethane and *p*-bromobenzeneazotribenzoylmethane behave in the same manner as *p*-nitrobenzeneazoacetyldibenzoylmethane (this vol., i, 662), changing into colourless isomerides when heated alone or with indifferent solvents. The coloured substances are azo-compounds,  $\text{NR}\cdot\text{N}\cdot\text{C}(\text{COR})_2\cdot\text{COR}$ , whilst the colourless isomerides are hydrazones,  $\text{COR}\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{COR})_2$ , which do not undergo the converse transformation in benzene, ether or chloroform at 160°.

*Benzeneazoacetyldibenzoylmethane*,  $\text{C}_{23}\text{H}_{15}\text{O}_3\text{N}_2$ , prepared by addition of diazobenzene chloride and sodium acetate to the enolic modification of acetyldibenzoylmethane in alcoholic solution at 0°, forms yellow crystals, m. p. 90°, evolving gas. The isomeric *hydrazone* crystallises in white needles, m. p. 188°.

*p*-Bromobenzeneazoacetyldibenzoylmethane,  $\text{C}_{23}\text{H}_{14}\text{O}_3\text{N}_2\text{Br}$ , forms amber-coloured, monoclinic crystals, m. p. 113°. The *hydrazone*,  $\text{C}_{21}\text{H}_{12}\text{O}_3\text{N}_2\text{Br}\cdot\text{N}\cdot\text{Ac}\cdot\text{N}\cdot\text{C}(\text{COPh})_2$ , crystallises in white needles, m. p. 218°, and when reduced with zinc dust and ammonia yields acet-*p*-bromoanilide. On treatment with sodium ethoxide at 0°, both isomerides yield *p*-bromobenzeneazodibenzoylmethane,  $\text{C}_{21}\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$ , crystallising in golden leaflets, m. p. 147—149°.

*p*-Bromobenzeneazotribenzoylmethane,  $\text{C}_{28}\text{H}_{19}\text{O}_3\text{N}_2\text{Br}$ , forms yellow crystals, m. p. 130—135°. The *hydrazone* crystallises in colourless needles, m. p. 220—221°, and is reduced by zinc dust and acetic acid to form benzo-*p*-bromoanilide.

[Combination of *o*-Diazo-oxides with 1:8-Dihydroxynaphthalene-3:6-disulphonic Acid.] FARBERKE VORM. MEISTER, LEONH. & COENIG (D.R.-P. 184689).—The nitro-*o*-aminophenols, containing the nitro-group in the para-position with respect to the amino-group, yield sparingly soluble, yellow diazo-oxides, which couple far more readily with 1:8-dihydroxynaphthalene-3:6-disulphonic acid (chrome

acid) in the presence of potassium hydroxide or carbonate is employed. The azo-derivatives obtained give various shades of blue on chrome-mordanted wool.

G. T. M.

**Etherification of Hydroxyazo-compounds by means of Methyl Sulphate.** AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [16, ii, 437—464].—As a rule, hydroxyazo-compounds can be converted quantitatively into the corresponding methoxyazo-derivatives by shaking their alkaline solutions for a short time with a slight excess of methyl sulphate. In some cases, for example, with azo-compounds derived from phenols in which the para-position is occupied by another substituent, the etherification is only effected on heating, and proceeds best when an absolute alcoholic solution of the alkali derivative of the hydroxyazo compound is treated with methyl sulphate.

This method has been applied to the preparation of the methyl ethers of benzeneazophenol, 2:4-bisbenzeneazophenol, benzeneazoguaiacol, m. p. 53—54° [Jacobson, Jaenicke, and Meyer gave m. p. 44.5—45° (*Ber.*, 1897, i, 143)], and the following new compounds.

The methyl ether of *o*-nitrobenzeneazoguaiacol,  $C_{15}H_{13}O_4N_3$ , separates from alcohol in reddish-brown crystals, m. p. 152°.

The methyl ether of  $\beta$ -naphthylazoguaiacol,  $C_{15}H_{10}O_4N_3$ , is deposited from alcohol in long, orange-red, acicular crystals, m. p. 103—105°.

The methyl ether of *p*-bromobenzeneazoeugenol,  $C_{17}H_{15}O_3N_2Br$ , separates from benzene in minute, pale-yellow crystals, m. p. 92—94°.

The methyl ether of *m*-xyleneazoeugenol,  $C_{15}H_{12}O_3N_2$ , forms minute, brick red crystals, m. p. 56°.

T. H. P.

**Esterification of Azo-derivatives of Hydroxy-acids by means of Methyl Sulphate.** AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 547—551. Compare preceding abstract).—

When an azo-derivative of *o*- or *m*-hydroxybenzoic acid is treated with rather more than 2 mols. of potassium hydroxide and rather more than 1 mole. of methyl sulphate, it yields a mixture of the esters  $N_2Ph \cdot C_6H_3(OH) \cdot CO_2Me$  and  $N_2R \cdot C_6H_3(OMe) \cdot CO_2Me$ . In the cases examined, the methoxy-acid,  $N_2R \cdot C_6H_3(OMe) \cdot CO_2H$ , was not detected.

Thus benzeneazosalicylic acid [ $OH : CO_2H : N_2Ph = 2 : 1 : 5$ ] yields:

(1) methyl 5-benzeneazo-2-methoxybenzoate,  $N_2Ph \cdot C_6H_3(OMe) \cdot CO_2Me$  [ $N_2Ph : CO_2H : OMe = 5 : 1 : 2$ ], which separates from alcohol in crystals, m. p. 63—64°; (2) methyl 5-benzeneazosalicylate,  $N_2Ph \cdot C_6H_3(OH) \cdot CO_2Me$ , is deposited from alcohol in yellow crystals having a metallic lustre, m. p. 162—165°.

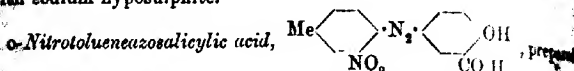
The *p*-chlorobenzeneazo-derivative of *m*-hydroxybenzoic acid gives:

(1) methyl 6-*p*-chlorobenzeneazo-3-methoxybenzoate,  $C_6H_4Cl \cdot N_2 \cdot C_6H_3(OMe) \cdot CO_2Me$  [ $C_6H_4Cl \cdot N_2 : CO_2Me : OMe = 6 : 1 : 3$ ], which separates from alcohol in orange-yellow crystals, m. p. 89—90°;

(2) methyl 6-*p*-chlorobenzeneazo-3-hydroxybenzoate,  $C_6H_4Cl \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2Me$ , which is deposited from alcohol in shining red crystals, m. p. 155°.

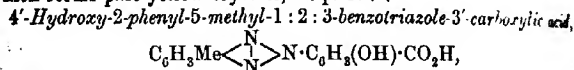
T. H. P.

**Reduction of *o*-Nitrotoluenesalicylic Acid by Means of Sodium Hyposulphite.** ECKHART GLASPERG and J. R. GUNAY (Ber., 1907, 40, 4205—4208. Compare this vol., i, 186).—Further investigation shows that the reduction of *o*-nitroazo-compounds by means of sodium hyposulphite does not always cease when the azo-imino stage is reached, the corresponding triazole compounds being sometimes obtained directly by further action. In other cases, the triazole compounds are produced together. Both the *o*-nitroazosalicylic acids dealt with in the present paper give triazole derivatives on reduction with sodium hyposulphite.



either by the interaction of diazotised *m*-nitro-*p*-toluidine and salicylic acid in alkaline solution or by the nitration of *p*-toluenesalicylic acid in concentrated sulphuric acid, crystallises from aqueous alcohol in felted masses of long, yellow needles, m. p. 213°. The acetyl derivative crystallises from aqueous alcohol in pale yellow needles, m. p. 167°.

*p*-Toluenesalicylic acid,  $\text{C}_8\text{H}_8\text{O}_3\text{N}_2$ , prepared either from the dye "flavazol," which is its sodium salt, or from diazotised *p*-toluidine and salicylic acid, crystallises from aqueous alcohol in brown leaflets, m. p. 212—213°, and yields an acetyl compound,  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , which forms pale yellow crystals, m. p. 157°.



prepared by reducing *o*-nitrotoluenesalicylic acid in alkaline solution by means of sodium hyposulphite, crystallises from alcohol or acetic acid in white needles, m. p. 276° (slight decomp.). Its acetyl derivative,  $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_3$ , crystallises from aqueous alcohol in slender, white needles, m. p. 198°.

The reduction of *o*-nitrobenzenesalicylic acid (compare Elbs and Keiper, Abstr., 1903, i, 662) in alkaline solution by means of sodium hyposulphite yields benzotriazole-2-salicylic acid (Elbs and Keiper, loc. cit.). T. H. P.

**Steric Hindrance.** HUGO KAUFFMANN and W. FRANCK (Ber., 1907, 40, 3999—4015. Compare Abstr., 1906, i, 841).—It is suggested in view of the hypothesis of the divisibility of valence that the steric hindrance observed with ortho-substituted compounds may arise from mutual interference of the partial valencies. The following cases of steric hindrance have been observed with ortho-substituted resorcinol dimethyl ethers. 2-Nitroresorcinol dimethyl ether is reduced only with great difficulty by zinc dust in alkaline solution. 2-Aminoresorcinol dimethyl ether cannot be acetylated by the ordinary methods, and does not form a benzylidene derivative; it is diazotised by nitrous acid, and reacts with carbon disulphide, forming a thiocarbamide only extremely slowly. The diazo-sulphate formed from 2-aminoresorcinol dimethyl ether is stable, can be recrystallised from alcohol, remains unchanged on prolonged boiling with water.

is a nitro-derivative when heated with fuming nitric acid, and is boiled with a solution of cuprous cyanide in potassium cyanide as a stable copper compound which again forms the diazo-salt on treatment with acids. On the other hand, substitution in the nucleus takes place readily; 2-nitroresorcinol dimethyl ether is easily nitrated and nitrated, and condenses readily with aldehydes. The resistance observed does not in any case amount to inhibition; extent depends on the reagent, since 2-aminoresorcinol dimethyl ether reacts only with great difficulty with acetic acid, acetic anhydride, or benzaldehyde, but readily enters into reaction with methyl carbimide or ethyl iodide.

2-Nitroresorcinol dimethyl ether is prepared in an 85% yield by the action of methyl sulphate on 2-nitroresorcinol in 10% aqueous sodium bromide solution at 70–80°; it remains almost unchanged when treated with alcoholic potassium hydroxide. When treated with a small amount of bromine in glacial acetic acid solution, it forms 2-bromo-2-nitroresorcinol dimethyl ether,  $C_8H_8O_4NBr$ , m. p. 55–56°, or in an excess of bromine the dibromo-derivative,  $C_8H_6O_4NBr_2$ , which crystallises in white needles, m. p. 100–101°.

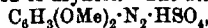
The action of fuming nitric acid on 2-nitroresorcinol dimethyl ether leads to the formation of two products. 2:4-Dinitroresorcinol dimethyl ether,  $C_8H_8O_6N_2$ , formed at the ordinary temperature, crystallises in yellowish-white needles, m. p. 72°, or after fusion and resolidification, m. p. 62°. 2:4:6-Trinitroresorcinol dimethyl ether, m. p. 125°, formed by the boiling acid, is identical with Hönig's phenyl acid dimethyl ether (Abstr., 1878, 727). Whilst the dinitro-ether is only slowly attacked by boiling aqueous sodium hydroxide, the trinitro-ether is rapidly hydrolysed, forming 2:4:6-trinitroresorcinol.

In presence of sulphuric acid, 2-nitroresorcinol dimethyl ether condenses with chloral hydrate, forming 3:3'-dinitro-2:4:2':4'-dimethoxydiphenyltrichloroethane,  $CCl_3 \cdot CH[C_6H_3(OMe)_2NO_2]_2$ , which separates from benzene-light petroleum in yellow crystals, m. p. 118–120°.

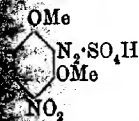
2-Nitroresorcinol dimethyl ether is reduced only to a small extent to fine dust in boiling alcoholic potassium hydroxide or by sodium amyl alcohol, but readily by iron powder in glacial acetic acid or stannous and hydrochloric acid, forming 2-aminoresorcinol dimethyl ether,  $H_2O_2N$ , which crystallises in white leaflets, m. p. 75°, b. p. 165–173 mm. The acetyl derivative,  $C_{10}H_{12}O_5N$ , is formed by heating the base with acetic anhydride in a sealed tube at 150–160° for ten hours; it crystallises in white leaflets, m. p. 81°, and is hydrolysed by dilute hydrochloric acid. 2:6:2':6'-Tetramethoxy-s-diphenylthiocarbamide,  $C_{17}H_{20}O_4N_2S$ , m. p. 170°, is formed in only small amount when the amine is boiled with carbon disulphide and alcoholic potassium hydroxide, but in slightly better yields if sulphur is employed in place of potassium hydroxide (compare Hugershoff, Abstr., 1899, i, 886). 2:6-Dimethoxy-s-diphenylthiocarbamide,  $C_{15}H_{16}O_2N_2S$ , m. p. 150°, on the other hand, is formed rapidly with slight development of heat when the amine is shaken with phenolthiocarbamide.

dimethyl ether with ethyl iodide in a reflux apparatus on the water-bath, is obtained as an almost colourless oil, b. p. 130°/12 mm. *Diethylchloride*,  $(C_2H_5O)_2N_2 \cdot H_2PtCl_6$ , was analysed. With sodium nitrite in acid solution, the base forms a dinitro-derivative,  $C_6H_3O_2N_2$ , which is obtained in yellowish-brown crystals, m. p. 108°.

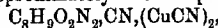
A soluble *dialzo-chloride* is obtained when 2-aminoresorcinol dimethyl ether is treated with sodium nitrite and hydrochloric acid at ordinary temperature and then heated gradually to 60—70°; nitrous gas is not evolved when the solution is nearly neutralised with sodium hydroxide and evaporated to dryness. The *dialzo-sulphate*,



prepared by diazotisation with amyl nitrite in alcoholic solution, forms yellow crystals, is stable when free from amyl nitrite, burns quickly on platinum, can be recrystallised from benzoyl chloride, and remains unchanged when boiled with water or hydrochloric acid, or when heated at 300° with concentrated sulphuric acid, but is decomposed by aqueous alkalis, forming resorcinol dimethyl ether. On addition of a concentrated solution of the diazosulphate to 50% aqueous sodium hydroxide, a white substance separates, which couples only slowly with alkaline  $\beta$ -naphthol, behaving therefore as an *anti-dialzo-oxide*. The *dialzo-salt* couples with  $\beta$ -naphthol in alkaline solution, forming 2:6-dimethoxybenzeneazo- $\beta$ -naphthol,  $C_{18}H_{16}(OMe)_2 \cdot N_2 \cdot C_{10}H_7 \cdot OH$ , which crystallises in red needles, m. p. 120—121°, and is not fluorescent. When boiled with fuming nitric acid, the *dialzo-sulphate* yields a



*nitro-derivative* having probably the annexed constitution, which couples with alkaline  $\beta$ -naphthol forming a dye,  $C_{18}H_{16}O_6N_2$ , crystallising in red needles, m. p. 162—163°. The *dialzo-perbromide*,  $C_6H_3O_2N_2Br_8$ , prepared by adding potassium bromide and aqueous bromine to the *dialzo-sulphate*, crystallises in needles, decomp. 120°, and loses bromine in contact with water slowly at the ordinary temperature, but quickly on heating. At the ordinary temperature, the *perbromide* changes slowly into a red substance, which couples to only a small extent. A yellowish-brown salt, having approximately the composition:



is formed by the action of cuprous cyanide in potassium cyanide solution on the *dialzo-sulphate* in presence of sulphuric acid, dissolved in hydrochloric acid, forming a solution which couples with  $\beta$ -naphthol and yields resorcinol dimethyl ether when heated with alkalis. A yellow substance, containing tin, formed by the action of stannous chloride and concentrated hydrochloric acid on the *dialzo-sulphate*, behaves in the same manner. 2-Iodoresorcinol dimethyl ether,  $C_6H_3OI$ , prepared by heating the *dialzo-sulphate* with concentrated aqueous hydroiodic acid, crystallises in white needles, m. p. 103°, and does not react with "active" magnesium. G. Y.

—Methods for the Removal of Proteins from Solution. From ROSE and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1907, 5, 365—367). Compare this vol., i, 667, and following abstract).—The precipitation

proteins by mastic suspensions is more rapid when the mastic is present in the solution. As the mastic, however, always carries down a large proportion of the protein, even from concentrated solutions, complete precipitation may be achieved by adding mastic several times at intervals. In many cases, precipitation by China clay is preferable to that by mastic. G. B.

**The Behaviour of Electrolytes in Mastic Precipitation.** MAX MICHAELIS, LUDWIG PINCUSOHN, and PETER RONA (*Biochem. Ztsch.*, 1907, 6, 1—16. Compare Abstr., 1907, i, 667).—A study of the extent to which electrolytes are carried down from a solution in which mastic flocculation occurs. The problem is of practical importance in connexion with the method of removing proteins, described in a preceding abstract. Acids produce flocculation in very small concentrations, and are not at all carried down by the precipitate. Ferric hydroxide is not an efficient precipitating agent, and is not carried either; baryta is more efficient, and is adsorbed to some extent. Mere traces of colloidal ferric hydroxide precipitate the acids, and are thereby completely adsorbed. Sodium and ammonium chlorides resemble acids in not being adsorbed at all, but are less efficient precipitants. Other metallic salts are still less efficient, and with those of the heavy metals there is partial adsorption of the bases. Urea, urea, glycine, and hippuric acid are not carried down at all. Very similar results were obtained with China clay instead of mastic. G. B.

**Rotatory Power of Proteins Extracted from Cereal Flours in Aqueous Alcohol.** LÉON LINDER and LOUIS AMMANN (*Compt. rend.*, 1907, 145, 253—255; *Bull. Soc. chim.*, 1907, [iv], 1, 968—974).—By fractional precipitation of wheat gliadin dissolved in 70% alcohol in alcohol or water, two gliadins were obtained,  $\alpha$ ,  $-81.6^\circ$  and  $\beta$ ,  $-92.7^\circ$ . The rotatory power of the mixed gliadins (twenty samples) varied between  $-81.6^\circ$  and  $-92.7^\circ$ .

Rye and barley yielded a protein, hordein,  $\alpha$ ,  $-137.5^\circ$ .

Two of the three maisins ( $\alpha$  and  $\beta$ ) obtained by Donard and Labbe (*Abstr.*, 1905, i, 215, 782) were separated from maize,  $\alpha$ ,  $-29.6^\circ$  ( $\alpha$ ) and  $-49.0^\circ$  ( $\beta$ ). N. H. J. M.

**The Swelling of Fibrin.** MARTIN H. FISCHER and GERTRUDE LOBE (*Amer. J. Physiol.*, 1907, 20, 330—342).—An attempt to explain the variable affinity of colloids for water on physico-chemical lines. As a physiological outcome, it is found that substances which are most effective in diminishing the amount of swelling of fibrin in hydrochloric acid are those which most retard gastric digestion. The absorption of water by frog's muscles is entirely analogous to the absorption of water by fibrin. W. D. H.

**The Products Obtained by Boiling Casein with 25% Sulphuric or Concentrated Hydrochloric Acid.** EMIL KERNHOLDEN and CASIMIR FUNK (*Zeitsch. physiol. chem.*, 1907, 53, 29—30).—The amount of glutamic acid produced by the hydrolysis of



casein with 25% sulphuric or concentrated hydrochloric acid is much the same, namely, some 10–11%, if the hydrolysis is continued for a sufficient length of time. Anhydrides of dipeptides are also formed in both cases; the amounts, however, are exceedingly small, under 1%. When sulphuric acid is used, the anhydride consists of a mixture of leucinimide and *l*-phenylalanyl-*d*-alanine anhydride, and probably *l*-leucyl-*d*-valine anhydride. The amounts of anhydride tend to increase as the time of heating is decreased. When hydrochloric acid is used, leucinimide alone is formed.

Amino-acids do not yield diketopiperazine when heated with concentrated hydrochloric acid.

J. J. S.

**Hydrolysis of the Sodium Salts of Casein.** LEON L. VAN SLYKE and DONALD D. VAN SLYKE (*Amer. Chem. J.*, 1907, 38, 613–626).—Determinations of the quantity of alkali hydroxide required for the neutralisation of casein give results which vary according to the indicator employed. Laqueur and Sackur (*Abstr.*, 1903, 1, 209) in determining the equivalent weight of casein, arbitrarily regarded phenolphthalein as giving correct results.

In the hope of obtaining a method of ascertaining the true neutralisation point, the electrical conductivity of solutions of varying amounts of casein in 100 c.c. of *N*/100 sodium hydroxide has been determined. Usually when an acid is added to a solution of a strong base, the conductivity gradually decreases until the neutral point is reached, and by plotting the conductivities as ordinates and the amounts of acid added as abscissae, a curve is obtained as a straight line sloping downwards to the neutral point, at which it breaks sharply. The curve for casein, however, like that for phosphoric acid, is concave and does not show any break. The minimum point is near that at which the solution is neutral to phenolphthalein, but cannot be regarded as representing the true point of neutralisation. E. G.

**Dissociation of Solutions of the Neutral Caseinates [Caseinogenates] of Sodium and Ammonium.** T. BRADSHAW ROBERTSON (*J. Physical Chem.*, 1907, 11, 542–552).—Neutral solutions of the sodium and ammonium salts of caseinogen (termed casein by the author) have been prepared by shaking the respective alkalis with excess of caseinogen and filtering, and the electrical conductivity of these salts in various dilutions has been measured at 25°. The variation of the conductivity with dilution is such as to justify the assumption that caseinogen behaves to alkalis as a weak tri-ambiprotic monobasic acid. From the conductivity results, on the assumption that no complex ions containing sodium are present, the value  $2.6 \times 10^{-5}$  cm./sec. is obtained for the velocity of the caseinogen ion, but, when the results for the ammonium salt are calculated on the same assumption, it is found that the sum of the velocity of the  $\text{NH}_4^+$  and protein ions is less than the known velocity of the  $\text{NH}_4^+$  ion alone. It follows that the solution of the ammonium salt contains complex ion-protein compounds in which the non-protein ion (in this case  $\text{NH}_4^+$ ) is not dissociated as such; the formation of such compounds is thus proved for the first time, although their existence had been foreseen by Loeb.

The dissociation constants for the sodium and ammonium salts of haemoglobin are 0.0395 and 0.0428 respectively. G. B.

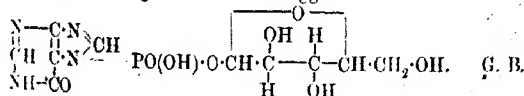
**Molecular Weight of Oxyhaemoglobin.** GUSTAV HÖRMER and HANS GÄSSER (*Chem. Zentr.*, 1907, ii, 816; from *Arch. d. physiol.*, 1907, 209—216).—By means of osmotic pressure measurements, the mol. weight of the haemoglobin from horses and cows was found to be 15,115 and 16,321 respectively, it being still doubtful whether these mol. weights are really different. The authors deduce from their osmotic pressure experiments that crystalline oxyhaemoglobin is composed of one mol. of haemoglobin combined with one mol. of oxygen. W. H. G.

**Paranucleo protagon.** MATTHEW STEEL and WILLIAM J. GIES (*Ann. J. Physiol.*, 1907, 20, 378—398).—This is the name given by Ulpiani and Lelli (Abstr., 1902, ii, 573) to a compound in the brain in which they believe the protagon is combined. It is resolved by alcohol into protagon and paranuclein. They further adhere to the idea that protagon is a definite chemical individual. The material is extracted from the brain with chloroform. On the lines of Gies' previous work, the present paper again deals with the non-existence of protagon as a chemical unit, and similarly it is shown that paranucleo-protagon is a mixture also; it contains other substances as well as the two mentioned by Ulpiani and Lelli, and the products left over with the strength and temperature of the alcohol used to decompose it. Probably none of the constituents of protagon are combined with a nuclein-like substance. W. D. H.

**Composition of Nucleic Acids of Thymus and Herring-Roe.** I. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, 53, 14—18; compare this vol., i, 168).—In addition to guanine, adenine, cytosine and thymine, episaccharic acid (this vol., i, 739) has been isolated from the nucleic acid of thymus by hydrolysis with concentrated nitric acid. The quinine salt,  $2C_{20}H_{24}O_2N_3C_6H_{10}O_8$ , crystallises well.

It is suggested that the remaining residue in the nucleic acid is  $C_{12}H_{10}O_7P_4$  and not  $C_{21}H_{41}O_{26}P_4$ , and the formula for the acid then becomes  $C_{43}H_{57}O_{30}N_{15}P_4$ . The residue,  $C_{21}H_{41}O_{26}P_4$ , is supposed on hydrolysis to yield a sugar and metaphosphoric acid. J. J. S.

**Inosic Acid.** CARL NEUBERG and B. BRAHN (*Biochem. Zeitsch.*, 1907, 5, 438—450).—Inosic acid is the only nucleic acid which can at present be obtained pure (as a crystalline salt). Hauser (Abstr., 1895, i, 39) stated that when hydrolysed it is decomposed into phosphoric acid, and probably a purine base and trihydroxyvaleric acid. The second of these products has now been identified as hypoxanthine, and the first as D-xylose. Hydrolysis takes place according to the equation:  $C_{12}H_{13}O_8N_4P + 2H_2O = H_3PO_4 + C_6H_{10}O_5 + C_6H_7N_3O_3$ . Inosic acid is optically active,  $[\alpha]_D^{20} - 18.5^\circ$ , a fact which has hitherto been overlooked. The following constitution is suggested:



...of ...  
...10, 345—370.  
The author has arrived independently and almost simultaneously to the same general conclusion as Neuberg and Brahn (preceding abstract), namely, that inosic acid is composed of a molecule of phosphoric acid and a molecule of hypoxanthine, which are united by an intermediate pentose molecule in such a way that the latter has lost its free aldehyde group. There is still some disagreement, or doubt, as to the nature of this pentose. The author, who did not observe the optical activity of inosic acid, obtained from it on hydrolysis a substance, m. p. 158—159°, which he regards as derived from *arabinose*. Whereas Neuberg and Brahn identify the sugar with *xylose*. The dextrorotation, which this latter substance might be expected to produce in the solution after hydrolysis, has, however, not been observed in either investigation.

A full account of the literature and details of a method of preparing crystalline barium inosate is given (yield 3 to 4 grams per kilo of meat extract used). In meat extract, the sugar of inosic acid occurs in the free state, probably owing to partial hydrolysis during manufacture.  
G. R.

**Tanning and Adsorption Compounds of Gelatin.** L. CRAMER (*Chem. Zentr.*, 1907, ii, 413—415; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 1, 353—364. Compare Biltz, *Abstr.*, 1904, ii, 331. A. and L. Lumière and Seyewetz, *Abstr.*, 1906, i, 916).—All metallic salts the solutions of which contain a colloidal hydroxide are capable of tanning gelatin. Dilute, but not strong, solutions of ferric chloride produce coagulation when added to a solution of gelatin. No coagulation occurs if a ferric salt is added to an ammoniacal solution of gelatin. Ferrous salts, potassium ferrocyanide, and ferrioxalate have no tanning action, whereas uranyl salts, auric chloride, and ceric sulphate tan readily. Copper salts and silver nitrate are adsorbed without coagulation. It is impossible to free gelatin treated with a solution of silver bromide in sodium thiosulphate from silver completely by washing; similarly, gelatin treated with mercuric chloride, mercuric iodide, lead iodide, lead nitrate, and barium chloride cannot be freed from these salts by washing.

Gum arabic and albumin behave like gelatin.

W. H. G.

**Alkaline Digestion.** HANS EULER (*Arkiv. Kem. Min. Geol.*, 1907, No. 39, 1—13. Compare this vol., i, 574).—Experiments on the action of pancreatin extract on glycylglycine in presence of small proportions of sodium hydroxide show that the pancreatin combines with a considerable part of the alkali, and, as the effect of the latter on the reaction is great, extracts of commercial pancreatin and trypsin, unless extremely active, are unsuitable for physico-chemical investigations on dipeptides. The results also show that Schütz-Borissow's rule does not hold for the alkaline digestion of dipeptides.

The pancreatin employed yielded 5.4% of ash, consisting principally of sodium pyrophosphate, probably derived from disodium hydrog. phosphate by heating. The velocity of digestion of glycylglycine by

creatin in presence of sodium hydroxide is not. The addition of sufficient disodium hydrogen phosphate to neutralise the phosphoric acid present originally. Also, this velocity is not lowered by more than 10% of its value by the addition of 0.1 gram of sodium arsenic anhydride, 0.12 gram of formaldehyde, or 0.1 gram of potassium azide per 100 c.c. of liquid.

The course of the decomposition of glycylglycine by the proteolytic action of soaked peas in presence of sodium hydroxide indicates that an excess of the latter is, in this case, far more completely neutralised than by erepsin.

The following results were obtained by the action of 4 grams of reactive erepsin on 100 c.c. of 0.1N-glycylglycine solution in presence of varying proportions of alkali:

concentration of alkali .....	0.035	0.04	0.05	0.06	0.070
reaction constant, $K \times 1000$ ...	5.0	7.0	8.3	8.0	6.5

From these results, the conclusion is drawn that alkaline digestive enzymes are not rendered active by the alkali, which accelerates their action partly by neutralising the substrate and partly by preventing the retarding effect of free decomposition products.

The hydrolysis of casein by erepsin is similar to that of glycylglycine. In the former case, however, the destruction of the enzyme is more important in comparison with the retardation caused by the decomposition products, whilst with glycylglycine the opposite holds. The reaction coefficient in the case of casein diminishes rapidly as the action proceeds, but the initial velocities are very nearly proportional to the concentrations of the enzyme. Such enzyme solutions, hence, cannot be regarded as heterogeneous systems.

It was further found that the conductivity of faintly alkaline casein solutions gradually diminishes, even in absence of enzyme.

The intensity of the action of erepsin varies for different dipeptides, the values of  $1000K$  being 58.4 for alanyl-glycine, 13.1 for leucyl-glycine, and 7.0 for glycylglycine.

The decomposition of glycine anhydride by alkali was studied by measuring the conductivity, which was found to diminish considerably. In the reaction proceeded, the alkali causing the opening of the ring and the formation of the sodium derivative of glycylglycine. By dilute hydrochloric acid, glycine anhydride is far more slowly decomposed, and here too the velocity rapidly diminishes owing to the combination of the acid with the decomposition products.

Experiments with germinating peas show that, during the ten days from the beginning of germination to the stage at which the lateral roots are developed, the quantity of enzyme capable of decomposing glycylglycine remains practically constant. The enzyme probably acts in the resting seed, either as active enzyme or as proenzyme. This is not the case with the other enzymes of germinating seeds, for instance, with those causing proteolysis.

T. H. P.

**Action of Arginase on Creatine and other Guanidine Derivatives.** HENRY D. DAKIN (*J. Biol. Chem.*, 1907, 3, 435-441).  
-Arginase is a specific enzyme for the exclusive hydrolysis of

Arginine or of substances containing the  $\epsilon$ -arginine group. Creatine and other guanidine derivatives structurally similar to arginine are incapable of hydrolysis by this enzyme. W. D. H.

**Specific Accelerating Action of Sodium Fluoride on the Coagulation of Milk by Vegetable Rennet.** C. GREGG (*Comp. rend.*, 1907, 145, 689-692).—The rate of coagulation of milk by vegetable rennet is first slightly accelerated, then retarded by the addition of increasing quantities of sodium fluoride; when the salt is present in the proportion of 30-60 mg. molecules per litre of milk, there is no coagulation, but the process begins again as the proportion of the salt is increased, the rate of coagulation being first accelerated, then retarded. The irregularity of these results is attributed to the disturbing influence introduced by the precipitation of the calcium salts present by the sodium fluoride. If a small quantity of sodium chloride is added to the mixtures, the results are comparable with those previously obtained, and show that the specific action of sodium fluoride is similar to that of sodium chloride. M. A. W.

**Systematic Investigation of Oxydases in Animal Tissues.** OCTAVE DONY-HÉNAULT and Mlle. J. VAN DEUREN (*Bull. Acad. roy. Belg.*, 1907, 537-638).—In the first part of this memoir, a résumé of current theories explaining catalytic oxidation is given, and the analogies between such actions and those due to oxydases in living tissues are detailed. Attention is then directed to the tests which have been applied by various investigators in ascertaining the occurrence of oxidising ferments in animal organs. Schmiedeberg's test, which consists in estimating the amount of salicylaldehyde converted into salicylic acid by an extract of the organ under investigation, has been fully examined, and it is found that it is liable to three sources of error. In removing the excess of salicylaldehyde as a preliminary to the estimation of the amount of acid formed, a saturated solution of sodium hydrogen sulphite is used, and it is found that this in presence of salicylic acid and ether leads to the formation of some sulphuric acid and organic acids, the latter being apparently produced from the ether. The alkalimetric estimation of the salicylic acid formed gives therefore results which are usually too high. Colorimetric estimation of the salicylic acid by means of ferric chloride only gives trustworthy results when the amount of acid is small and there are no other free acids present. Eliott's method (*Abstr.*, 1889, 195), which depends on the conversion of the salicylic acid into tribromophenol, gives good results in the case of pure mixtures of the aldehyde and acid, but it appears to be impossible to extract the whole of the acid by means of ether from albuminous solutions, such as aqueous extracts of organs, so that even using this method the results obtained are low, but a modified form of the method, described in detail in the original, was eventually adopted as the best available.

In the experiments, an extract of calves' livers in salt (0.2%) or sodium-fluoride (0.65%) solution, was used. It was found that the oxidation of salicylaldehyde to salicylic acid by such extracts takes

are best in the absence of oxygen, and that the velocity of the reaction varies greatly and irregularly when the concentration of the extract varies and is conditioned mainly by the concentration of the aldehyde. The oxidising power of the extracts diminishes spontaneously on keeping, and this diminution in activity usually occurs more rapidly in presence of air, or when the temperature is raised. Some extracts remain active after being heated to 80°, whilst others show a marked lessening of activity after exposure to this temperature. These observations are insufficient to enable a decision to be arrived at as to whether the oxidation is due to an oxydase or is merely catalytic, but the authors are inclined to adopt the latter alternative.

The last portion of the memoir is devoted to a criticism of the work of Abelous and his collaborators (Abstr., 1896, ii, 119; 1898, 35; 1900, i, 268, ii, 226; 1903, ii, 560, 561, 678; 1904, ii, 188) on the subject, and in this connexion it is pointed out that all the extracts used in the present set of experiments contained a small amount of oxyhæmoglobin, which rapidly disappeared when the extracts were exposed to air, but persisted for some time in its absence, which would probably not have been the case if an oxydase had been present in the solution. Salicylaldehyde is not oxidised by oxyhæmoglobin, so that the latter cannot be the source of the action used in the oxidation of the aldehyde by organic extracts. It is suggested that as oxyhæmoglobin can exist in dilute solution in vacuum for some days, the current view that the mechanism of oxygen exchange brought about by hæmoglobin is mainly physical is not strictly accurate.

T. A. H.

**Animal Peroxydases.** ERNST VON CZYHILARZ and OTTO VON BARTH (*Beitr. chem. Physiol. Path.*, 1907, 10, 358—389).—An attempt is made to extend to animal oxydases the sharp distinction drawn by Chodat and Buch between (vegetable) direct oxydases and peroxydases, which latter only oxidise in the presence of hydrogen peroxide or of some other peroxide. The guaiacum reaction of blood is due to hæmatin and not to a true peroxydase. The difficulty of completely removing blood from the tissues makes guaiacum tincture an unsuitable reagent for the detection of peroxydases. For tissues containing blood, the liberation of the presence of hydrogen peroxide of iodine from an acidified solution of potassium iodide should be employed.

A spectro-photometric method, based on the oxidation to malachite-green of the leuco-base, has been worked out and employed in the measurement of the velocity of peroxydase action. A graphical representation of the results obtained by this method shows that the oxidation by hæmatin proceeds at a uniform rate, whereas the velocity of that due to animal peroxydase gradually falls off to zero. The peroxide reaction is much more dependent on the concentration of the leuco-base than is the hæmatin reaction.

The oxidation of ammonium sulphide by oxyhæmoglobin is not accelerated by catalase, and there is no ground for the belief that the latter enzyme has a direct oxidative action, as supposed by Ewald (this vol., ii, 184).

G. B.

...antagonism ... and ...  
 ...HERLITZKA (*Ann. P. Chem.*, 1907, (5), 184). According to Ewald (this vol. ii, 184), the dissociation of oxyhaemoglobin is a phenomenon connected with the partial pressure of the oxygen of which the relation existing between oxyhaemoglobin and haemoglobin is a function. This being so, catalase is capable of increasing the velocities of two chemical reactions of different nature, one being independent and the other dependent on the partial pressure of the oxygen, and the one irreversible and the other reversible. (Compare Herlitzka, this vol., i, 102). Objections are raised to Ewald's results. Further experiments by the author lead to the conclusion that there exists an antagonism between the action of catalase on the rate of haemoglobin, or, in general, of the oxydases with respect to the oxidation of guaiacum resin by peroxides, that is, with respect to the formation of active oxygen. Within certain limits, the greater the concentration of the catalase, so much the greater must be the concentration of the peroxydases to produce oxidation. Thus there is a direct proof of the protective action exerted by catalase towards the peroxydases destroying and rendering innocuous the peroxides in the organism.  
 T. H. P.

**Thiophenol-5-chlorophosphines and their Derivatives.**  
 AUGUST MICHAELIS and G. LINUS JANKE (*Ber.*, 1907, 40, 3419—3421). Compare Michaelis, Abstr., 1903, i, 379; Autenrieth and Hildebrand, *Monatsh.*, 1898, i, 419, 476).—*Thiophenylchlorophosphine*,  $\text{SPH}\cdot\text{PCl}_2$ , obtained by heating thiophenol and phosphorus trichloride in a flask fitted to a reflux condenser, forms a somewhat thick, colourless liquid,  $n_D^{20} 1.257/10 \text{ mm.}$ ,  $D_4^{25} 1.2560$ . It fumes in contact with the air and has a disagreeable odour. When left exposed to the air for twenty-four hours, hydrogen chloride is evolved and a crystalline mass consisting of triphenyl trithiophosphite,  $\text{P}(\text{SPH})_3$ , and phosphorous acid is obtained; but when the chlorophosphine is poured into water, a violent reaction occurs, and the products are hydrochloric and phosphorous acids and thiophenol. A thiophosphorous acid has not been obtained. With alcohol, the products are hydrogen chloride, thiophenol, and triethyl phosphite, and with sodium ethoxide, triethyl trithiophosphite, triethyl phosphite, and sodium chloride. The thiophenylchlorophosphine reacts with chlorine yielding phenyl disulphide and phosphorus trichloride. Thiophenol and phosphoryl chloride react with phosphorus trichloride, phenyl disulphide, and phosphoric acid. *Thiophenylthionchlorophosphine*,  $\text{SPH}\cdot\text{PSCl}_2$ , obtained by heating the thiophenylchlorophosphine with sulphur at  $120^\circ$  for five hours and distilling the product under reduced pressure, forms a thick, colourless liquid with an aromatic odour,  $b. p. 168-170/16 \text{ mm.}$ , and is not appreciably acted on by water.

The quantitative yield of triphenyl trithiophosphite,  $\text{P}(\text{SPH})_3$ , is obtained when phosphorus trichloride is heated with three equivalents of thiophenol at  $150^\circ$  in an oil-bath. It crystallises from ether in short, monoclinic prisms or from alcohol in pointed crystals,  $m. p. 76-77^\circ$ . With concentrated sulphuric acid, it yields thiophenol and phosphorous acid, and the same products are formed when the trithio-

yl derivative is heated with water or alcohol, and the phenyl trithiophosphate readily combines with oxygen, forming an anion, but is decomposed by chlorine yielding phenyl disulphide and phosphorus trichloride.

*Triphenylphosphine oxide*,  $O:P(SPh)_3$ , obtained by the action of hydrogen peroxide on the phosphine, crystallises from ether in strongly acting, monoclinic prisms, m. p.  $115^\circ$ . It may also be prepared by the action of phosphorus oxychloride on sodium thiophenol, but the duct described by Schwarze (*J. pr. Chem.*, 1874, [ii], 10, 254) is probably phenyl disulphide.

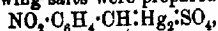
*Triphenylphosphine sulphide*,  $S:P(SPh)_3$ , crystallises from alcohol plates, m. p.  $86^\circ$ . It is obtained by the direct addition of sulphur carbon disulphide solution at  $120^\circ$ , or by the action of phosphorus trichloride on sodium thiophenol.

*Triphenylphosphine selenide*,  $Se:P(SPh)_3$ , crystallises from ether pale yellow, monoclinic plates, m. p.  $95^\circ$ . Secondary chlorophosphines have not been prepared. J. J. S.

**Mercury Compounds from Nitrotoluenes.** ARNOLD REISSNER *et al.*, 1907, 40, 4209—4226. Compare this vol., i, 908).—Although aromatic amines and phenols readily admit of the entry of mercury into their molecules, nitrobenzene has but slight tendency to act in this way. The author finds, however, that *o*- and *p*-nitrotoluenes are readily converted into mercury derivatives when boiled with mercuric oxide in presence of sodium hydroxide, the mercury in these cases entering the side-chain. The compounds yielded by nitrotoluene and 2:4-dinitrotoluene have not been obtained in a pure state, but from *o*-nitrotoluene two well-characterised chemical individuals have been prepared.

*o*-Nitromercuribenzylic chloride,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot HgCl$ , obtained by adding dilute sodium hydroxide solution containing *o*-nitrotoluene in suspension with precipitated mercuric oxide, is precipitated from ammoniacal solution by hydrochloric acid in bundles of colourless needles, m. p.  $145$ — $146^\circ$ .

*o*-Nitrodimercuribenzylidene oxide,  $NO_2 \cdot C_6H_4 \cdot CH \begin{smallmatrix} Hg \\ Hg \end{smallmatrix} O$ , obtained by protracted boiling of sodium hydroxide solution, *o*-nitrotoluene, and mercuric oxide, is precipitated from acetic acid solution by excess of sodium hydroxide in dark yellow, crystalline masses decomposing at above  $220^\circ$ . The following salts were prepared: the *sulphate*,



crystallising in pale yellow, broad needles or plates; *basic sulphate*,  $NO_2 \cdot C_6H_4 \cdot CH(Hg \cdot OH)Hg_2 \cdot SO_4$ , forming a heavy, orange-yellow powder; *chloride*,  $NO_2 \cdot C_6H_4 \cdot CH(HgCl)_2$ , a pale yellow, amorphous compound; *hydroxychloride*,  $NO_2 \cdot C_6H_4 \cdot CH(HgCl) \cdot Hg \cdot OH$ ; *nitrate*, and *nitrite*,  $NO_2 \cdot C_6H_4 \cdot CH(Hg \cdot NO_2)_2$ .

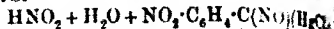
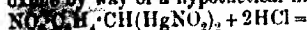
*o*-Nitrodimercuribenzylidene oxide is partially decomposed by hydrogen sulphide into mercuric sulphide and *o*-nitrotoluene. By zinc dust and sulphuric acid, it is reduced to *o*-toluidine and mercury. When heated with nitrous acid, it gives *o*-nitrobenzaldehyde, which is



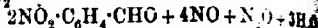
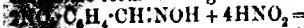
also formed together with a small proportion of *o*-dinitrotoluene,



When treated with nitric acid. When treated in the same way with nitric and hydrochloric acids, it is converted into approximately molecular proportions of *o*-nitrobenzaldehyde and its oxime; the dimeric form formed by the nitrous acid is converted by hydrochloric acid into the oxime by way of a hypothetical nitroso-derivative:



and the latter:  $+ 2\text{HCl} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{NOH} + 2\text{HgCl}_2$ , one half of the oxime formed being then transformed into the aldehyde as follows:



Towards acids and alkalis, *o*-nitrodimercuribenzylidene oxide is, in general, very stable, but, when boiled with 20% hydrochloric acid solution, it is transformed into anthranil,  $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{O}$ .

The action of chlorine, best in presence of excess of hydrochloric acid, on *o*-nitrodimercuribenzylidene oxide yields *o*-nitrobenzylidene chloride,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHCl}_2$ , which, in a slightly impure condition, is a faintly red oil, b. p. 150–151°/10 mm. Similarly, the action of bromine yields the corresponding bromide and that of iodine, *o*-nitrobenzylidene iodide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHI}_2$ , which crystallises from alcohol in yellow prisms, m. p. 70–72°.

The interaction of *p*-nitrotoluene and precipitated mercuric oxide in presence of sodium hydroxide yields *p*-nitrodimercuribenzylidene oxide which was not obtained pure and which is converted into *p*-nitrobenzoic acid by the action of dilute nitric acid.

Similarly, 2:4-dinitrotoluene is converted almost quantitatively into 2:4-dinitrodimercuribenzylidene oxide, which is converted into mercuric sulphide and 2:4-dinitrotoluene by hydrogen sulphide, into 2:4-dinitrotoluene by 10% hydrochloric acid, and into 2:4-dinitrobenzoic acid by concentrated nitric acid.

T. H. P.

